EVALUATION OF NOVEL VISCOELASTIC SYSTEM AS A POTENTIAL CHEMICAL EOR METHOD IN CARBONATE RESERVOIRS

BY

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Dedicated to

my beloved parents

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جزاكم الله خيرا

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LIST OF SYMBOLS

A : cross sectional area in cm^2

Ant/VES: Anionic surfactant/Viscoelastic surfactant

$°API$: American Petroleum Institute

ASP : Alkaline surfactant polymer

B : Formation volume factor

Btu : British thermal unit

$°C$: Degree Celsius

Ca^{2+} : Calcium ions

Cl^{-} : Chloride ions

Cat/VES: Cationic surfactant/Viscoelastic surfactant

cEOR : Chemical Enhanced Oil recovery

CMC : Critical Micelles Concentration

cP : centi Poise

C.W : Combined water

dP : Differential pressure in $atmosphere$

D.W : Deionized water

E_D : Displacement efficiency

EOR : Enhanced oil recovery

E_V : Volumetric sweep efficiency

$°F$: Degree Fahrenheit

ft : Feet

F.W : Formation water

G' : Storage modulus

G" : Loss modulus

gm : gram

h : net thickness

$HCIP$: Hydrocarbon in place

HCO^{-3} : Carbonate ions

HLB : Hydrophilic- Lipophilic Balance

HPAM : Hydrolyzed polyacrylamide

IFT : Interfacial tension

IPV : Inaccessible pore volume

k : absolute permeability in $Darcy$

k_o : Effective oil permeability

K_{ro} : Relative permeability to oil

k_w : Effective water permeability

L : length of the core in cm

mD : milli Darcy

Mg^{2+} : Divalent magnesium ions

MGPP : Molecule Geometry Packing Parameter

m$\frac{N}{m}$: milli Newton/meter

M.R : Mobility ratio

Na^{+} : Sodium ions

N_c : Capillary number

Non/VES: Nonionic surfactant/Viscoelastic surfactant

OOIP : Original oil in place

P : Polymer

PF : Polymer flooding

φ : Porosity

P_c : Capillary pressure

PCC : Powdered Calcium carbonate

PPM : Parts per million

psi : Pounds per square inch

PV : Pore volume

PVT : Pressure, volume, temperature

q : flow rate in $\frac{cm^3}{s}$

QSPR : Quantitative Structure- Property Relationship

Q_o : Oil production in bbl

R : ratio of interaction energy of surfactant and oil in interface layer

RF : Recovery factor

$\frac{rad}{s}$: Radian per second

SF : Surfactant flooding

SP : Surfactant polymer

SPI : Surfactant polymer interaction

S/VES : Surfactant/Viscoelastic surfactant

SO^{-4} : Sulphate ions

S_{or} : Residual oil saturation

S_w : Water saturation

S.W : Sea water

S_{wc} : Connate water saturation

TGA : Thermo gravimetric analysis

TOC : Total organic carbon

TPM : Triphenoxy methanes

μ : Shear viscosity in cP

μ_o : Oil viscosity in cP

μ_W : Water viscosity in cP

v : Velocity of fluid in $\frac{cm}{s}$

VES : Viscoelastic surfactant

VES/P : Viscoelastic surfactant/Polymer

VES/R : Viscoelastic surfactant/Reducing agent

ω : Angular frequency $\frac{rad}{s}$

WLM : Wormlike Micelles

γ : Shear rate in 1/s

Zwit/VES : Zwitterionic surfactant/Viscoelastic surfactant

ABSTRACT

Full Name : Madhar Sahib Azad

Thesis Title : Evaluation of Novel Viscoelastic System as a Potential Chemical EOR Method in Carbonate Reservoir

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Carbonate reservoirs characterized by low permeability, high concentration of divalent ions, high temperature and salinity contains almost 60% of the oil and gas resources. Chemical EOR is one of promising EOR technique that has attained wide spread attention due to the hike in oil price. Surfactant flooding, polymer flooding, surfactant polymer flooding (SP), and alkaline surfactant polymer flooding (ASP) are the common variants of chemical EOR methods. Surfactant flooding might result in the poorer sweep efficiency due to the channeling of the low viscous injected surfactant. Polymer flooding apart from its inability to mobilize the oil could results in poorer sweep efficiency too in low permeable carbonate reservoirs. It is due to the inability of polymer's slug to get into low permeable region of carbonate reservoirs because of its high hydrodynamic radius. SP flooding and ASP flooding are prone to chromatographic separation of slugs that could make the overall process ineffective. Further most of the conventional surfactants and polymers are susceptible to high salinity and temperature encountered in carbonate reservoirs. The Viscoelastic fluid's resistance to high salinity; high temperature and high divalent ions concentration and its ability to provide both displacement and sweep efficiency via its viscoelastic nature along with its shear thinning nature could be

exploited. Three VES were tested for its oil recovery potential with 57,000 ppm saline water. The optimum one among the three is chosen for further study. The effect of parameters on shear viscosity and IFT of optimum VES is measured. The ability of VES to combat formation water salinity in poorly preflushed region and high permeable region of the carbonate reservoirs are analyzed through rheological studies. Different formulations namely Viscoelastic surfactant system (VES), Surfactant/Viscoelastic Surfactant system (S/VES), and Viscoelastic surfactant/Polymer system (VES/P) have been tested for its Viscosity/IFT ratio. The optimum systems were subjected to thermal stability tests and core flooding. Thermal optimization of VES is done by combining VES with reducing agent (VES/R). The ability of thermally stable VES to exploit thin heavy oil reservoirs in tandem with hot water is studied through reservoir simulation.

Rheological characterization of the optimum VES indicate the potential of it to combat complexities in carbonate reservoirs and also its potential over polymer as the mobility control agent. VES as a single system outperform S/VES and VES/P systems and the core flooding done with 1.5 PV of VES systems reduce the residual and remaining oil saturation to 0.23. The tested VES forming wormlike micelles (WLM) can be a potential EOR fluid for high salinity, moderate temperature and fractured carbonate reservoirs. It applicability for high temperature reservoirs could be improved by preventing long term thermal degradation through the VES/R systems. Simulation studies done based on dual mobility control concept indicate that thermally stable VES that could form hybrid EOR method with hot water might open new vistas for heavy oil recovery in thin viscous heavy oil reservoirs where conventional steam flood and polymer flood completely fails.

ملخص الرسالة

الاسم الكامل: مظهر صاحب ازاد

عنوان الرسالة: دراسة تقيمية لمواد ذات اللزوجة المرنة كطريقة كيميائية محتملة لتحسين استخلاص النفط من الصخور الكربونية

التخصص: هندسة البترول

تاريخ الدرجة العلمية: نوفمبر 2014

تتميز مكامن الصخورالكربونية التي تحتوي على 60% من احتياطيات البترول والغاز بنفاذية منخفضة، و تركيز عالي للايونات ثنائية التكافؤ، و درجة حرارة و ملوحة عاليتين. ويعتبر تحسين استخلاص النفط كيميائيا في هذه الصخور احد التقينيات الواعدة التي حظيت باهتمام واسع نتيجة لارتفاع سعر النفط في السنوات الماضية. حيث أن الغمر بالمؤثر السطحي (السيرفاكتنت)، أو الغمر بالبوليمر، أو الغمر بالبوليمر و المؤثر سطحي ، أو الغمر بالمؤثر السطحي و القلوي و البوليمر معاً وهذه هي اشهر خيارات التحسين الكيميائي للاستخلاص. حيث أن الغمر بالمؤثر السطحي قد يؤدي الى كفاءة أقل عندما ينتقل المؤثر السطحي المحقون ذو اللزوجة المنخفضة في قنوات الصخور الكربونية دون مسامات الصخر ذاته. وكذلك الغمر بالبوليمر قد يؤدي الى كفاءة ازاحة اقل في مكامن الكربونات ذات النفاذية المنخفضة و ذلك نتيجة لعدم قدرة كتلة البوليمر من الدخول في الاجزاء قليلة النفاذية في مكامن الكربونات نسبة لكبر قطرها الهيدروداينميكي. كما أن الغمر بالبوليمر ليس له القدرة على تحريك النفط ذو اللزوجة العالية. وعند النظر الى الغمر الثلاثي باستخدام البوليمر و المؤثر سطحي و المؤثر القلوي فان هذا المزيج عرضة لانفصال الكتل الكروموتوغرافي مما قد يؤدي الى عدم فعالية عملية الاستخلاص. بالاضافة الى ذلك، فان المؤثر السطحي و البوليمر التقليديين لديهما حساسية عالية للملوحة و الحراة العاليتين الموجودة في مكامن الصخور الكربونية. لذلك تعتبر مقاومة المائع المرن اللزج (viscoelastic ~ VES) للحرارة و الملوحة العاليتين، و التركيز العالي للايونات ثنائية التكافؤ و قدرته على توفير كفاءة ازاحة و احلال عن طريق طبيعته المرنة اللزجة التي تتناوب بين الحالتين حسب الضروف الخاجية المحيطة. لذلك تم في هذه الدراسة اختيار قدرة استخلاص النفط لثلاث مؤثرات سطحية مرنة لزجة (VES) في مياة تحت نسبة ملوحة عالية تصل الى 57.000 جزء من المليون. وبعد الاختبارات الاولية تم أختيار المادة الامثل

من الثلاث لاجراء دراسات اضافية. حيث تم قياس تاثير التركيز ودرجات الحرارة على اللزوجة و التوتر السطحي للمؤثر السطحي المرن اللزج الافضل. كما أن قدرة المؤثر السطحي المرن اللزج على مكافحة ملوحة المياه الطبقية في المناطق التي لم يتم غمرها جيدا و المناطق ذات النفاذية العالية في مكامن الكربونات تم تحليلها بالدراسة الريولوجية. كما تمت دراسة تركيبات مختلفة للمؤثر السطحي المرن اللزج مع السيرفاكتنت (S/VES)، و البوليمر (VES/P) لاختبارنسبة اللزوجة الى التوتر السطحي فيها، ومن ثم اختيار التركيبة الامثل التي تم تعريضها لاختبارات الاستقرار الحراري، و الغمر، و اختبارات الامتصاص الساكن. وتم التوصل الى تحسين الخواص الحرارية للمؤثر السطحي المرن اللزج بدمج المؤثر السطحي المرن اللزج مع عامل تخفيض (VES/R).

وبالنظر الى السمات الريولوجية للمؤثر السطحي المرن اللزج الافضل بين المواد الثلاث التي تمت دراستها توحي بقدرة هذه المواد على التغلب على التعقيدات والشقوق في مكامن الصخور الكربونية و ايضا افضليتها على البوليمر كعامل تحكم بالحركية. تفوق المؤثر السطحي المرن اللزج (VES) على المؤثر السطحي مع السيرفاكتنت (S/VES)، و المؤثر السطحي المرن اللزج مع البوليمر (VES/P) عندما تم استخدام 1.5 الحجم الفراغي للمؤثرات السطحية المرنة اللزجة في اختبار غمر العينات حيث انخفض نسبة النفط المتبقي الى 23%. من المعروف أن المؤثر السطحي المرن المختبر يكون مائع يحتوي على مذيلات دودية الشكل (wormlike micelles) في حالة الملوحة العالية، درجة الحرارة المتوسطة و مما يساعد على رفع اللزوجة وهي نتيجة ايجابية لعمليات الحقن في المكامن الكربونات المتشققة. كما أن امكانية تطبيق استخدام المؤثرات السطحية المرنة اللزجة في المكامن عالية الحرارة يمكن ان يتحسن بمنع التراجع الحراري طويل المدى باستخدام عامل تخفيض (VES/R). ومن حيث قدرة المؤثر السطحي المرن اللزج و المستفر حراريا لاستخلاص النفط الثقيل من المكامن ذات السمك القليل، تمت دراسة نمذجة تحاكي المكامن النفطية الثقيلة بوجود مياه ساخنة، حيث اظهرت النتائج نسبة انتاج أعلى. حيث أن دراسات النمذجة بناء على مبدا تحكم الحركية المزدوج تشير الى ان المؤثر السطحي المرن اللزج المستقر حراريا و الذي يشكل نظام تحسين استخلاص نفطي هجين مع الماء الساخن يمكن ان يفتح وجهات نظر جديدة للنفط الثقيل في المكامن ذات السماكة المنخفضة التي يفشل فيها الغمر بالبخار او البوليمر التقليديين.

CHAPTER 1

INTRODUCTION

1.1 EOR add Oil Reserves

World Energy consumption through fossil fuels is more than 85%. Around 32 billion of barrels of oil are produced each year. Since the global energy demand and consumption forecast to grow rapidly during the forthcoming years, the possible solution to meet this need lies in sustaining the production or increasing the reserves from the existing field (Sheng 2010). Reserves can simply be stated as the product of resources and recovery factor. The new discoveries are becoming increasingly difficult as almost most of the basins had been explored already. Unexplored basin are mostly in environmentally sensitive areas such as in Arctic and Antarctica (Muggeridge, Cockin et al. 2014). So, improving the recovery factor from the existing field is a viable option to increase the reserves. In U.S.A, the total volume of oil discovered until 1993 is around 536 billion barrels, with the total produced being around 162 billion barrels (30% of total discovered) and reserves being around 23 billion barrels (4% of total discovered). Hence the 66% of the already discovered oil are yet to be recovered (Green and Willhite 1998). Conventional recovery methods cannot recover it due to various factors that mainly include higher capillary force and oil viscosity (Muggeridge, Cockin et al. 2014). Hence if EOR methods can recover alteast half of the remaining (176 billion barrels) then the recoverable reserves could be doubled. On a similar global analysis, 2 trillion barrels of oil can then be considered as the reserve (Sheng 2010).

Carbonate reservoirs contains 60% of the world oil and gas resources (Han, AlSofi et al. 2013). These resources can be the potential reserves with the improved recovery factor through EOR technologies. However, carbonate reservoirs are characterized by complex features such as the low permeability, huge fractures, and high concentration of divalent ions, high temperature, and high salinity etc. These possess the challenges for any EOR method which is implicative from the lesser number of successful EOR projects associated with carbonate when compared with sandstone (Manrique et al., 2010). However, if the potential chemical formulation is designed optimally, carbonate reservoirs can be exploited. Chemical EOR for carbonate reservoirs has not been studied much (Han, AlSofi et al. 2013). But the increased oil price in recent times has enticed the oil companies to invest more in EOR particularly in chemical EOR to extend their applicability to harsh reservoirs. Viscoelastic surfactant (VES) flooding is one such option for chemical EOR in carbonate reservoirs.

1.2 Stages of Oil Recovery

There are 3 stages of oil recovery. It includes the primary recovery, secondary recovery and tertiary recovery.

Primary recovery:

The oil is produced under the natural drive. The recovery factors are generally less than 30% (Kokal and Al-Kaabi 2010). Three major drive mechanisms contributing to the primary recoveries are: solution gas drive , gas cap drive and water drive

The solution gas drive reservoir depends on expanding gas bubbles from the gas dissolved in the subsurface oil to force the oil through the reservoir and into the well (Hyne 2014). A solution gas drive tends to be the relatively inefficient among the three primary recovery techniques. As the bubble point is reached, this become very inefficient. As long as the oil has dissolved gas, it could be mobilized easily. Once the gas evolves the viscosity of oil increases and complicates its flow. Hence it is imperative to initiate IOR/EOR processes in advance. An exceptional case is certain foamy heavy oil reservoirs whose solution gas drive mechanism can lead to the nucleation of heavy oil that could result in higher production (Maini, Sarma et al. 1993)

The Gas Cap drive is an oil field drive mechanism in which the pressure of the gas in the gas cap above the oil forces the oil into the oil wells (Hyne 2014). Gas-Cap drive is relatively an efficient driving mechanism. These reservoirs can be supplemented with pressure maintenance through gas injection process in gas cap.

The Water drive uses the pressure of water beneath an oil reservoir forces the oil into the wells. Water drive is a very efficient drive mechanism (Hyne 2014). The reservoir pressure remains near original pressure during production until the wells water out. This type of reservoirs can be supplemented by pressure maintenance through water flooding.

Secondary recovery:

An older term used for any process used to restore oil production from a reservoir in which the primary drive mechanism and reservoir pressure have been depleted. Gas injection and water flood are the examples. Common flooding patterns include five-spot,

inverted – five spot, nine-spot, inverted nine-spot etc. secondary techniques can recover up to 30-50% of oil (Kokal and Al-Kaabi 2010).

Gas injection: the injection of Carbon dioxide, Nitrogen or natural gas into the subsurface oil reservoir to maintain or restore reservoir pressure (Hyne 2014). In a saturated pool with a free gas cap, the gas is injected into the free gas cap. In an unsaturated pool, the casing head gas is directly injected into the oil.

Water flooding: an engineering method used to produce more oil from a reservoir after the oil is produced from its natural reservoir drive (Hyne 2014). Water is pumped down the injection wells which either can be drilled for that purpose or converted from producing wells. The injected water displaces the oil the reservoir and drives it to the producing wells. The water flood can be initiated either before or after primary production from natural reservoir drive has been completed. Recovery factor is 15-20%. In carbonate reservoirs, water flooding may not be efficient due to the excessive channeling of injected water through thief zones or fractures resulting in poor sweep efficiency. Further, the duration of water flooding is also crucial, as the persistent water flooding for extended time may lead to the increment in water saturation that might result in the stronger IFT and consequently higher capillary pressure. Care has to be taken to ensure, that implemented water flooding would be conducive to the augmented water flooding optimally with design chemicals to mobilize and sweep the oil.

Tertiary recovery:

The third stage of oil recovery in most of the reservoir, also called as Enhanced oil recovery involves the injection of slugs that could change the property of reservoir fluids

to increase the recovery factor. Sometimes it starts as the primary recovery in heavy oil reservoirs. It can be subdivided into thermal EOR, chemical EOR and miscible EOR. The overall recovery using EOR methods can be as high as 50% to 80% (Kokal and Al-Kaabi 2010). However, the oil productions through EOR methods are very low in the range of just 3 million barrels of EOR oil per day compared to overall production of 85 million barrels. EOR production is just 3.5% of total oil production (Kokal and Al-Kaabi 2010).

1.3 Classification of EOR methods

EOR can be classified in to three broad categories

Thermal EOR:

It involves the injection of heat energy into the heavy oil reservoir to heat and displace the viscous crude oil (Green and Willhite 1998). Steam flooding, cyclic steam stimulation and fire flooding are the major thermal EOR methods. Among the 3 million barrels of daily EOR oil produced, thermal EOR methods alone produce 2 million barrels (Kokal and Al-Kaabi 2010). The production mainly comes from regions possessing huge quantity of heavy oil reserves such as Canada, Venezuela, and Indonesia etc. Depending on the oil viscosity, certain thermal EOR methods have to be implemented right from the initial stage. Thickness of the reservoirs is the major factor restricting the steam flooding applications. However, thin reservoirs are accounting for huge heavy oil reserves (Azad, Sultan et al. 2014) need special attention. One possibility is to formulate Hybrid EOR method comprising thermally stable VES and hot water. The simulation studies of it are reported in this work.

Chemical EOR:

It involves the injection of formulated chemicals into the depleted reservoirs to mobilize the trapped oil as much as possible. Chemical EOR methods can give both microscopic displacement efficiency and macroscopic sweep efficiency. Among the 3 million barrels of daily EOR oil produced, chemical EOR methods are producing around 0.33 million barrels (Kokal and Al-Kaabi 2010). China is the lone country that got significant production from chemical EOR methods. Surfactant flooding, polymer flooding, surfactant polymer flooding, alkali surfactant polymer flooding are the major chemical EOR methods. Among the EOR methods, this has the strong potential for enhancing the EOR applicability in complex reservoirs such as the carbonate reservoirs prevalent in Middle East and complex heavy oil reservoirs. It is due to the fact, the scope for optimization of slugs with optimized chemicals (VES, the living polymer) is higher when compared with the steam and gases and hence it provides the better opportunity for exploiting complex reservoirs. Hence, VES is studied for its potential as an EOR fluid in this research.

Gas EOR:

It involves the injection of hydrocarbon/non hydrocarbon gases into the deeper reservoir to enable miscibility with the reservoir oil. Among the 3 million barrels of daily EOR oil produced, Carbon dioxide flooding produce around 0.33 million barrel (Kokal and Al-Kaabi 2010). U.S.A and Canada are the prominent regions benefitted with Carbon dioxide flooding. Another 0.33 million barrel of EOR oil is due to hydrocarbon gas injection. Libya, Canada, U.S.A are the countries benefitted by it (Kokal and Al-Kaabi

2010). Gas EOR as a single method may not be efficient in heterogeneous carbonate reservoirs due to the channeling and over run problems associated with low viscous, less dense and highly mobile gases. So a mobility control agent should be injected along with gases to prevent any such problem that doesn't warrant good sweep efficiency. Mobility control agent could be VES which has the advantage of providing IFT reduction to induce miscibility along with good sweep. Though, Viscoelastic surfactant can be a part of any EOR methods, its applicability as a chemical EOR fluid in carbonate reservoirs is the focus of this research.

1.4 EOR: What, When, Why, How and Where?

What is EOR?

Enhancement in oil production by means of injecting external fluids to drive the reservoir fluid towards the production wells with controlled mobility ratio.

Why EOR?

- The oil industries could not guarantee new discoveries
- New discoveries lie in deep offshore, remote forests and complicated areas
- EOR oil is cheaper than new oil
- Production from unconventional resources is expensive than production from known brown field by EOR
- Recovery factor from unconventional resources is uncertain.

When EOR?

- Loss of gas means loss of energy, better to start EOR/IOR before attaining bubble point pressure
- Chemical EOR is preferred earlier just after water flooding.
- Most of the heavy oil reservoirs needs EOR method as early

Where EOR?

- Formation type precludes some EOR methods such as carbonate reservoirs are not the candidate for conventional thermal and EOR methods (Manrique et al., 2010).
- Off shore EOR operations requires higher expense and longer development plan.
- Prize matters a lot and it is determined by reservoir volume and remaining oil saturation

$$HCIP = A * h * \varphi * (1 - S_w)/B \quad \text{..... (1)}$$

Where

HCIP= Hydrocarbon in place

A = Area of reservoir determined by structural mapping

h = net reservoir thickness determined by formation evaluation

φ= porosity determined by formation evaluation, coring

S_w= water saturation determined by tracer, logs, core analysis

B = Formation volume factor determined by fluid samples and PVT analysis

- Avoiding extremes, it includes
  a. Very high gross- to – pay ratio

b. Small areal extent

c. Highly heterogeneous reservoirs

d. Thin pay

e. Very deep reservoirs

f. Very high viscous oil

Enabling EOR applicability in these extremes is a challenge for all the EOR operators and research companies. In this work, we are investigating some of it.

- Economic , geo-political and management policy criteria
  a. Current oil prices
  b. Environmental considerations
  c. Government incentives such as tax and royalty holidays

How EOR?

Based on technical screening criteria, a specific EOR process has to be chosen for the particular candidate reservoir

- Reservoir containing light oil and moderate depth are suited for chemical EOR methods. However high salinity and fractures limits the chemical EOR applicability in carbonate reservoirs.
- Reservoir at shallower depth containing heavy oil are suited for thermal methods
- Reservoir at deeper depth containing light oil is suited for miscible methods.
- Horizontal well may address some problems associated with vertical wells in EOR. It includes

a) Insufficient well exposure to formation can be mitigated by drilling horizontal wells which provides higher sweep efficiency especially targeting the tight carbonate formation
b) Poor injectivity associated with vertical wells can be solved drilling horizontal wells that require lower injection pressures. Injectivity in low permeable portion of carbonate formation can be solved by it.
c) Vertical wells may lead to higher pressure draw down that may cause coning or cusping which can be prevented by drilling horizontal wells
d) Some EOR method such as steam flooding with vertical wells in thin reservoirs could be uneconomic, that could be improved by using horizontal wells. polymer flooding with horizontal wells proves to viable for heavy oil recovery (Tabary, Zaitoun et al. 2013; Delamaide, Zaitoun et al. 2014) .

1.5 EOR Recovery Concepts

Residual oil and bypassed oil are the two types of oil left behind after primary/secondary recovery techniques. The analysis of residual oil is important in low permeable reservoirs. The analysis of bypassed oil or the unswept oil is more of concern in heavy oil recovery and fractured reservoirs. Capillary number can explain the residual oil saturation concept and mobility ratio concept can be used to study the bypassed oil (Azad, Sultan et al. 2014). In this research, optimum VES system is chosen based on viscosity/IFT ratio, a form of capillary number and simulations works are done based on novel dual mobility control concept derived from mobility ratio.

Mobility ratio:

Mobility ratio (M.R) is defined as the ratio of mobility of displacing fluid to the mobility of displaced fluid (Green and Willhite 1998).

$$M.R = \frac{k_w/\mu_W}{k_o/\mu_o} \quad \ldots\ldots\ldots\

Capillary number

Capillary number (N_c) is defined as the ratio of viscous force to capillary force (Green and Willhite 1998).

$$N_c = \frac{\vartheta * \mu}{\sigma} \quad \ldots\ldots\ldots\

applicable to heavy viscous oil. Carbon dioxide flooding is more applicable to light oil at greater depths. Chemical flooding applicability lies in between. As per the EOR screening criteria proposed by (Taber, Martin et al. 1997), the chemical EOR methods are not preferred for carbonate reservoirs and heavy oil reservoirs containing oil viscosity of more than 150 cP. Also they concluded that steam flooding is the dominant EOR process and they dint see any scope for chemical EOR until the oil price goes high. Apart from considering the reservoir and crude oil properties for determining the possible EOR method, the price of oil is also crucial (Kokal and Al-Kaabi 2010). In 1997, the price of 1bbl of crude oil was around 18$ where as in 2013, the average oil price is around 89.34$. So with this hike in price, the operators can afford to spend in developing advanced EOR methods that are showing potential especially in harsh reservoirs where most of the conventional EOR methods fails. VES flooding is one such method. In this research, we are investigating the potential of VES to redefine certain EOR screening criteria through rheological, IFT, simulation, thermal stability and core flooding studies.

1.7 Overview and Challenges of Chemical EOR in Carbonate Reservoirs

Carbonate reservoirs are characterized by low permeable region, huge fractures, and high concentration of divalent ions, high temperature, and high salinity etc. Low permeability precludes the entry of EOR slugs into it. Huge fractures provide the easy conduit for the EOR slugs to pass through thereby reducing the sweep efficiency. High salinity and divalency causes the precipitation of chemical slugs and higher temperature causes the hydrolysis.

Most the reservoirs including complex carbonates may be the good candidate for chemical EOR methods provided if the chemical formulation is designed optimally. However the applicability of chemical EOR for carbonate reservoirs has not been studied much (Han, AlSofi et al. 2013).Also the conventional chemical EOR methods especially with anionic surfactants are not readily applicable for positively charged carbonate reservoirs. But the increased oil price in recent times has changed the fortune to expend dollars in developing the advanced EOR methods. The chemical EOR process can be explained by capillary number. Capillary number is the ratio of viscous forces to interfacial forces. High capillary number leads to low residual oil saturation. Surfactant could reduce the interfacial forces while polymer could increase the viscous forces. Among the chemical EOR methods, surfactant polymer flooding could be the suited one for carbonate reservoirs as long they are stable at the harsh conditions. But conventional surfactants and polymer carries the problem of precipitation and hydrolysis at harsh conditions (Seright 1983; Lyons and Plisga 2011). Alkaline Surfactant Polymer (ASP) cannot be applied in carbonate reservoirs due to the unfavorable interaction between divalent ions in the rock and the injected alkaline solutions (Lyons and Plisga 2011). Alkali reacts with the reservoir oil to generate in-situ surfactants and the reaction is contingent upon having the acid number in the range of 0.2mg KOH/g of oil (Lyons and Plisga 2011). Conventional Polymer flooding (PF) alone cannot contribute to IFT reduction (Green and Willhite 1998). Surfactant flooding (SF) can increase the relative permeability of water but may not provide effective mobility control (Hirasaki and Pope

1974). Surfactant Polymer flooding (SP) provides both microscopic and macroscopic displacement efficiency (Green and Willhite 1998; Gao, Towler et al. 2010). However there exists the chromatographic separation problems associated with the combined flooding involving surfactants and polymers (Li, Shi et al. 2009; Lyons and Plisga 2011).

Challenges for Chemical EOR in Carbonate Reservoirs

The **Figure 1** depicts the dominant applicability of chemical and thermal EOR in sandstone than in carbonate. Generally EOR methods are well established in sandstone reservoirs. As per the screening criteria proposed by (Taber, Martin et al. 1997), carbonate reservoirs are not the preferred candidate for the chemical EOR methods. It is due to the following:

a. Heterogeneity

Carbonate reservoirs are characterized by low permeability (Ehrenberg and Nadeau 2005). The low permeable nature of the reservoirs results in higher capillary pressure and limited scope for the viscous EOR slugs to enter inside for sweeping the oil. Polymer with its higher hydrodynamic radius cannot get inside the tight zones thereby could leave lot of oil unswept and immobilized. So using flexible, shear thinning VES could be an option to combat low permeable problems. Viscoelasticity of VES also might help in dragging the oil from low permeable region.

Carbonate reservoirs are characterized by high fractures (Ehrenberg and Nadeau 2005). The presence of fractures and thief zones also complicates the application of chemical EOR in carbonate reservoirs (Han, AlSofi et al. 2013). The expensive slugs injected might channel through the fracture, resulting in lower sweep efficiency. This is the case

with steam flooding and chemical flooding, where the injection fluids tends to bypass easily. Possible techniques used in the past to combat the adverse effects due to fracture includes foam (Austad and Milter 1997), inducement of wettability change (Seethepalli, Adibhatla et al. 2004) etc. However each process has its limitations. Foam is susceptible to brine (Maini and Ma 1985) and possess poor long term stability (Dahanayake, Chabert et al. 2011). Wettability alteration process cannot be controlled manually by selecting flow rates as it's an imbibition process dependent implicitly on capillary pressure characteristics of matrix (Dahanayake, Chabert et al. 2011). So using VES as a diverting fluid can be an option.

b. Harsh Conditions

Harsh conditions refer to the hostile environment for the injected chemicals. Salinity and temperature are the harsh conditions limiting the applicability of chemical EOR in carbonate reservoirs. Higher salinity causes the precipitation of the surfactants and higher temperature causes the poor thermal stability of slugs especially polymers. Unlike the stimulation process, EOR process is long term one that entails the holistic planning in selecting the chemicals that could sustain the harsh conditions. The salinity- temperature analyzed by (Han, AlSofi et al. 2013) plot implying the current research limits in Middle East is presented **(Figure 2).** Most of the Middle East carbonate reservoirs with high salinity and temperature are not the best candidate for conventional chemical EOR. Development in the chemical formulation could expand the applicability. Fortunately, VES is chemical which need harsh conditions to perform. Hence VES is explored in this research as an EOR fluid.

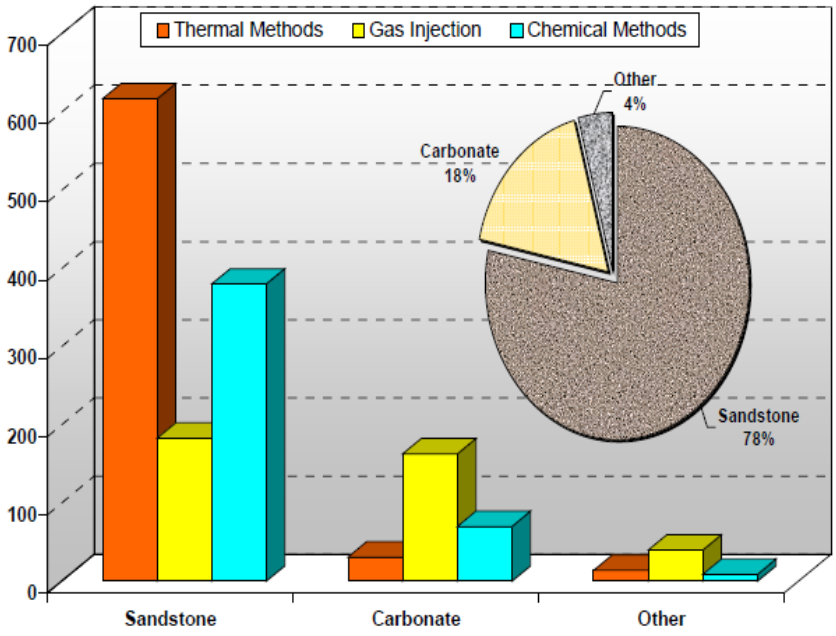


Figure 1: EOR statistical report

(Manrique 2010)

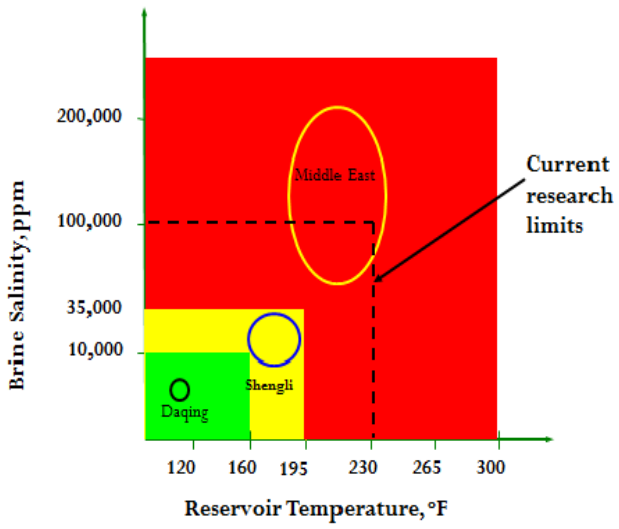


Figure 2: Temperature salinity plot implying the current research limits

(Han 2013)

1.8 Viscoelastic Surfactant as an EOR Fluid

Viscoelastic nature offered by certain fluids such as high concentrated polymer can lead to both microscopic and macroscopic efficiency. Though, injecting high concentration polymer makes it viscoelastic and may increase the microscopic displacement efficiency, it may lead to severe injectivity issue (Morvan, Degre et al. 2012). Carbonate reservoirs characterized by low permeability (Ehrenberg and Nadeau 2005) in particular may suffer more due to higher molecular weight polymer injection. An alternate option is using surfactant providing viscoelastic nature. Viscoelastic nature is believed to be result from a different type of micelle formation than the usual spherical micelles formed by most surfactants (Dahanayake, Chabert et al. 2011). Viscoelastic surfactant forms rod like micelles, worm like micelles or cylindrical micelles. The viscoelastic nature of the surfactant can be tested by swirling the solutions and visually observing whether bubbles created by the swirling recoil after the swirling is stopped (Dahanayake, Derian et al. 2008). These surfactants with viscosifying nature could generate micelles in favorable conditions. These micelles could grow as long as few tens of micrometers generating huge viscosity (Candau and Oda 2001). These micelles with higher viscosity can sweep the larger area thereby could increase areal sweep efficiency. So the overall recovery efficiency which is the multiple of displacement and sweep efficiency could be enhanced. Addition of non-viscoelastic surfactant (polymeric or non-polymeric) to the flooding fluid can impart additional IFT reduction or lesser mobility ratio. So VES, S/VES, VES/P systems have been studied individually in this research. Deeper reservoirs, heavy oil reservoirs and carbonate reservoirs are not the preferred candidate for chemical EOR

methods. Deeper reservoirs characterized by high temperature causes hydrolysis of chemicals, Heavy oil reservoirs characterized by the high oil viscosity leads to unfavorable mobility ratio and carbonate reservoirs characterized by low permeability , high salinity, high temperature leads to the excessive channeling of injected fluid, hydrolysis and precipitation. Carbonate reservoirs, prevalent in Kingdom and Middle East has been considered as the candidate reservoir for investigating the potentiality of VES as an EOR fluid in this research.

1.8.1 Special Properties of VES

VES possess certain properties that make it in an ideal EOR fluid. It include

1. Dual function of IFT reduction and viscosity (Berger and Berger 2008),(Azad and Sultan 2014)
2. Reversible Shear thinning (Sultan, Azad et al.2014), (Brand, Hansch et al. 2014)
3. Salinity resistance and divalency resistance (Berger and Berger 2008)
4. Elasticity for diversion (Gomma 2012)
5. Elasticity for dragging oil (Degré, Morvan et al. 2011)
6. Thermal stability (Berger and Berger 2008), (Degré, Morvan et al. 2011)
7. Preferential breakage of WLM structure upon contacting oil (Berger and Berger 2008)

1.8.2 VES as an EOR fluid in Complex Carbonate Reservoirs

Carbonate reservoirs possessing the greatest challenge for chemical EOR methods can be exploited by viscoelastic surfactant that has special properties. Viscoelastic surfactant is the self-assembling surfactant that contributes to the displacement and sweep efficiency

through the formation of wormlike micelles. WLM expands at favorable conditions leading to effective mobility control. Conditions are ascertained individually which is one of the objectives of thesis. Favorable conditions are in fact the harsh conditions that restrict the chemical EOR applicability in carbonate formations. VES's known for its positive response towards salts and temperature (Degré, Morvan et al. 2011) is studied in detail. VES though can't reduce the IFT significantly, still could reduce the residual oil saturation drastically (Brand, Hansch et al. 2014). Viscoelasticity and shear thinning are the important recovery factors associated with it. Fractures in carbonate provide the easy conduit for the injected slug, thus reducing the sweep efficiency of the overall EOR process.

Carbonate reservoirs are characterized with low permeability. Low permeable carbonate reservoirs possess one of the critical challenges of not letting the EOR slug easily to contact its residential oil. Polymer, the mobility control agent in particular cannot sweep those regions. Without sweep efficiency, the efficient displacement efficiency cannot be expected. So it's the polymer, the mobility control agent has to be reckoned. VES being a living polymer can provide the alternate option. It can relieve stress temporarily due to its structure held by weak molecular interaction. The fluid relieved from stress can penetrate the low permeable region with ease. VES can deform and reform upon applying and removing stress. Unlike polymer whose back bone consists of strong covalent bond, VES being held together by weak intermolecular forces provide the EOR researchers the option of both shear thinning and shear thickening. Shear thickening is essential for mobility control. Due to the ability of VES to change its behavior in accordance to prevailing situation, it is called living polymer. This is ascertained in the work .Core

flooding done on low permeable core using VES gives an excellent recovery. The pressure drop monitored while flooding also indicate the shear thinning of VES.

Fractured Carbonate reservoirs consist of two distinct elements; a fracture network and a low permeable region. Fluids can be transmitted easily through high permeable fracture network but fracture porosity is very less. However micro porous matrix consists of oil bearing porous rock that exhibits low permeability, low conductivity but higher porosity and oil saturations. Generally, hydrocarbon production is less in fractured reservoirs. During primary production, the natural reservoir pressures declined quickly leaving more than 90% oil in place. And even secondary production in the form of water flooding could not recover substantial amount of oil in the fractured reservoirs. It could be due to tendency of injected water to travel only through fracture thereby recovering the little oil left in fracture. Also the injected water may break through easily resulting in higher water-oil ratios. Further, the injected water cannot permeate in to the low permeable region to displace the trapped oil. The injected water cannot interact with oil in the matrix which is oil-wet. Micro porous matrix even could not spontaneously imbibe or absorb water. So a lot of oil is left behind in micro porous carbonate rocks.

One way to increase the water permeation in to micro porous matrix of the carbonate reservoir is to change the wettability of the rock from oil wet to water-wet**.** Anionic surfactants could change the wettability (Seethepalli, Adibhatla et al. 2004) and hence could recover more oil by creating a water-wet condition in the area near the fracture face. Upon such alterations, the injected aqueous phase could penetrate some distance into the micro porous matrix and thereby pushes some of the oil in the pores. But these imbibition processes are heavily dependent on the capillary pressure characteristics of the

porous rock matrix. Manually the processes cannot be controlled by selecting pressure or flow rates.

Another approach to recover the huge reserves of oil in the matrix is through foam (Novosad and Mannhardt 1989). Foam formed by aeration of a mixture of surfactant and water exhibits higher viscosity which reduces the mobility of the water/surfactant system into high permeable zones or large fractures effectively closing them off and/or providing a barrier to entry. With these altered conditions, the next slug of foam can be introduced along with surfactant solution to penetrate into micro porous to reduce the IFT between the water and oil thereby mobilizing it. But main problems with these method is the poor long term stability of foam, that the foam dissipates relatively quickly diminishing their efficacy in blocking high permeable, fingering prone large fractures.

So it would be desirable to have a method for enhancing the permeation of injected aqueous fluid through the low permeable carbonate rocks while substantially reducing the permeation through low porous fractures. Having VES as the EOR fluid facilitates it. Initially VES can be injected at high concentration to plug the fracture or high permeable region. Higher concentration gives higher solidity or elasticity due to the entanglement (Chellamuthu and Rothstein 2008). The elasticity is needed for diverting the fluids (Gomaa, Cutler et al. 2012). The dynamic studies done through the rheometer measures it. Having blocked it, low concentration of VES can be injected that could get inside the low permeable region through Brownian motion (Chellamuthu and Rothstein 2008). The released oil can internally break the VES's solidity to an extent through which it can travel towards the production well. Poor long term thermal stability of VES can also be an internal breaker. The properties that are essential for it include elasticity, shear

thinning, and internal breaking tendency of VES which are ascertained in this work through rheology.

1.9 **Problem statement**

Screening criteria evolved over the years (Taber, Martin et al. 1997) were being used as the reference to determine the applicability of various EOR methods. Each EOR methods need specific oil and reservoir properties (Lyons and Plisga 2011). Oil properties such as gravity, viscosity, composition and reservoir properties such as permeability, oil saturation, thickness, depth, formation type and temperature dictates the type of EOR method that the particular reservoir need. Among the major EOR methods, chemical EOR is the promising one whose applicability can be extended to wide variety of reservoirs. **Figure 3** depicts the ranges of applicability for different EOR methods based on depth and oil viscosity. It is clear that chemical EOR applicability lies in between thermal and gas EOR methods. Chemical EOR has the major limitation that it cannot be applied to reservoir possessing certain properties.

1. Deeper Reservoirs

   With depth, reservoir temperature increase. Above the depth of 9000 ft, the chemical EOR methods are not preferred. High temperature causes the hydrolysis of the injected chemicals. It affects stability of injected chemicals particularly polymer.

2. Carbonate reservoirs

   Carbonate reservoirs containing 60% of the oil resources are characterized by low permeability, high salinity, high divalency high temperature and fractures. Low

permeable carbonate reservoirs doesn't permit the entry of EOR fluids inside it. It causes poor sweep efficiency. In fractured carbonate reservoirs, the injected fluid tends to bypass through the high permeable region leaving lots of oil in the low permeable region. Thus heterogeneity causes the channeling of the injected slugs and could drastically reduce the sweep efficiency. Also carbonate reservoirs contains high concentration of divalent ions. At high temperature, surfactants used for chemical flooding tend to precipitate when exposed to high concentration of divalent cations. Polymer undergoes severe degradation at harsh conditions. Further, surfactant as single slug leads to channeling and injecting polymer as single slug doesn't mobilize the oil. Employing surfactant polymer flooding on a long term basis carries the risk of chromatographic separation in the harsh reservoirs. Investigating the potential of optimum stable viscoelastic surfactant as the chemical EOR method in these reservoirs through various approach is the focus of this research. The approach includes rheology, IFT, thermal stability and core flooding.

3. Heavy oil reservoirs

   Reservoir containing oil whose viscosity is greater than 35 cP are not preferred for surfactant flooding and whose viscosity is greater than 150 cP are not preferred for polymer flooding (Taber, Martin et al. 1997). Heavy oil accounts for more than 8 trillion barrels. Thermal methods such as steam flooding, cyclic steam stimulation have been used as the EOR methods to recover heavy oil. But certain reservoir conditions such thin reservoir, deeper reservoir makes thermal methods economically unviable. Polymer flooding belonging to non-thermal

chemical EOR method has the limitation of sweeping oil of above 150 centi Poise. Viscous fingering is the common problems associated with polymer flooding. A simulation study is carried out to compare the potential of VES flooding/ hot water, polymer flooding and steam flooding in thin viscous heavy oil reservoirs.

Advancement of chemical EOR methods can expand the circle depicted in **Figure 3** into ellipse as shown by bold ellipse. That is, the applicability of chemical EOR methods can go beyond 9000 ft. depth and 150 cP oil viscosity. But this requires detail investigation and recommended for dissertated studies with heavy oil in future. Chemical EOR methods capable of providing both microscopic displacement and macroscopic sweep efficiency, if optimized can be applied to deeper, carbonate and heavy oil reservoir. VES known for its thermal stability and divalency resistivity could be exploited for extending the chemical EOR applicability in these complex reservoirs. Further, viscoelastic property of VES and its compatibility with surfactant and polymer can be tailored to synergize the overall effect (IFT reduction and mobility control) thereby enhancing the applicability of chemical EOR methods. VES's applicability as the chemical EOR slug in low permeable carbonate reservoir with light oil is the focus of this thesis research. A complementary simulation is conducted to advocate the applicability of thermally stable VES for thin viscous heavy oil reservoirs where conventional methods fails.

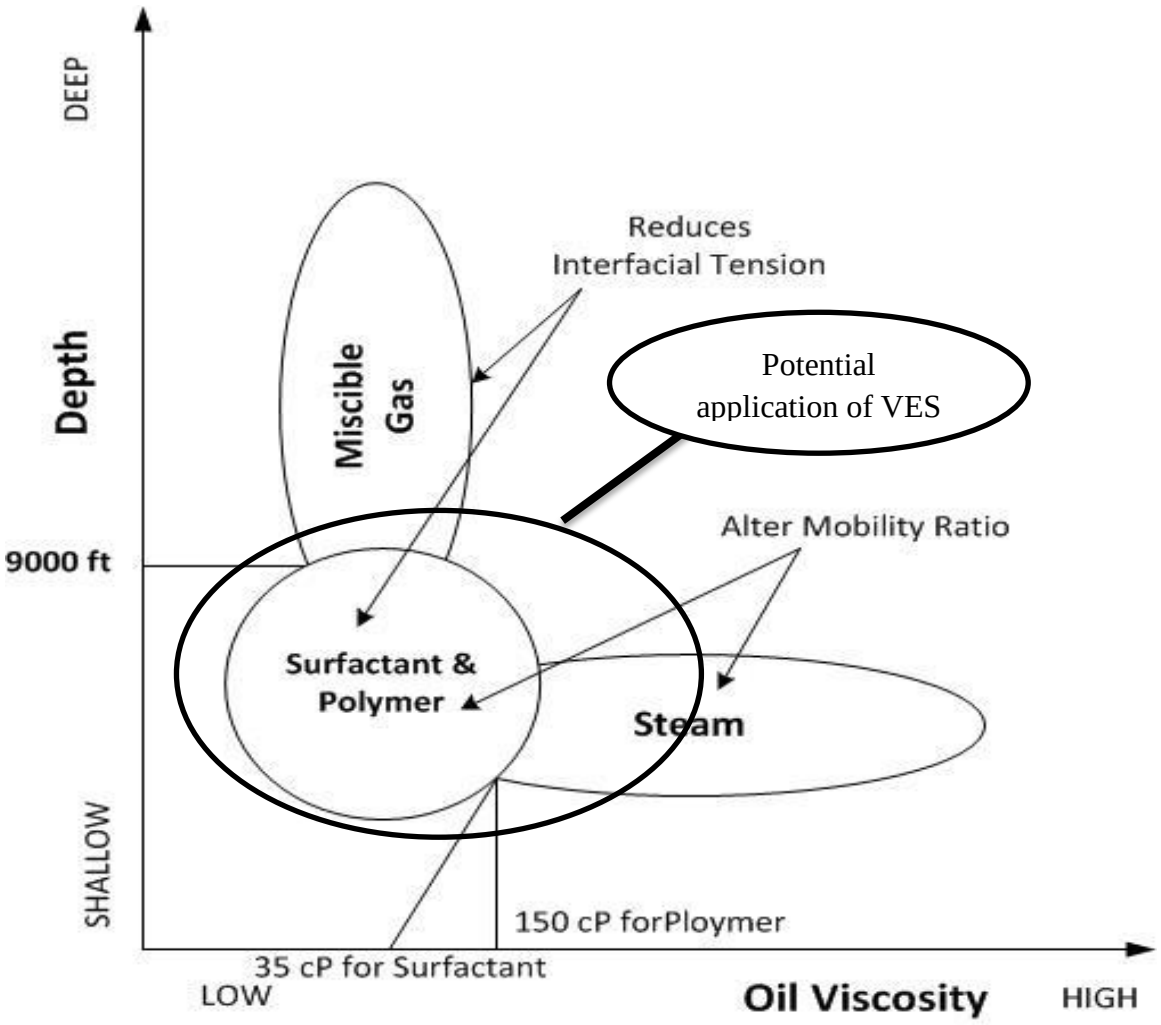


Figure 3: EOR applicability based on Depth vs. Viscosity plot

1.10 VES for Complex Heavy Oil Reservoirs (A Simulation Study)

Complex heavy oil reservoirs include thin heavy oil reservoirs and naturally fractured heavy oil reservoirs. Thin viscous heavy oil reservoirs possess the greater challenges for both thermal and chemical EOR methods. Heat losses and oil fingering are the major problems associated with steam flooding and polymer flooding in thin viscous heavy oil reservoirs. VES being thermally stable (Berger and Berger 2008), (Davies, Ketner et al. 2006)and (Degré, Morvan et al. 2011) can combine synergistically with hot water to recover heavy oil in thin heavy oil reservoir.

1.11 Objectives of the Thesis

The objective of the thesis is to test and evaluate the potential of VES as an EOR fluid in carbonate reservoirs. Following are the step by step objectives

1. To screen the optimum VES that is sustainable at the harsh conditions encountered in carbonate reservoirs.
2. To perform rheological characterization on optimum VES to
    - Study the effect of various parameters on WLM growth
    - compare the potential of VES and polymer
    - analyze the potential of optimum VES in addressing the problems due to high salinity and fractures
3. To perform IFT characterization on the optimum VES
4. To study the oil recovery potential of VES, S/VES and VES/P systems
5. To determine and optimize the thermal stability of optimum VES
6. To determine the oil recovery potential of VES through core flooding

7. To advocate the potentiality of VES/Hot water hybrid EOR method in thin, viscous heavy oil reservoirs through reservoir simulation studies where steam and polymer flooding fails.

1.12 Thesis Organization

In this thesis, the 1st introductory chapter started with the review stressing the importance of EOR for satiating the global energy need. It proceeded with an introduction about different stages of oil recovery, different kinds of EOR methods and the recovery potentials, mechanisms and concepts associated with it. Then an introduction about EOR screening criteria and possible modification sought through this research was stated in it. Then an introduction about the chemical EOR methods in carbonate reservoirs was stated along with their limitations. The challenges posed by carbonate reservoirs were elaborated. VES, a well-established stimulation field was deemed to be a potential option for carbonate reservoirs possessing such challenges. It unique properties were ascertained. Then the problem statement was defined and objectives that are intended to cover in this thesis are mentioned. The methodologies that are adopted for achieving these objectives are elaborated in Chapter 3.

Chapter 2 contains the literature review that cover the basics of chemical EOR and its variants followed by the literatures emphasizing the successful application of chemical EOR in sandstone and the challenges precluding the chemical EOR applicability in carbonate reservoirs. These are listed in sections from 2.1 to 2.3. Then sections 2.4 to 2.6 briefs about the EOR using viscoelastic polymer and the limitations associated with it. Then the detailed literature review about viscoelastic surfactant usage as an EOR fluid is presented in section 2.7. At the end of each review, the module of our work is included to

emphasize how this research is going to be different and advanced from the previous ones. It is then followed by the literatures augmenting the possible extension of chemical EOR to complex reservoirs such as carbonate and thin heavy oil reservoirs upon optimization in sections 2.8 and 2.9.

Chapter 3 includes the methodology adopted to accomplish the tasks. The over view of the integrated approach carried out is detailed under the section 3.1. As some experiments such as IFT and rheological measurements are being repeatedly used for various studies, the description of all the equipment is outlined in the section 3.2.1. Section 3.2.2 lists the materials used in the research. The procedure for preparing the sea water, formation water and VES, S/VES and VES/P solutions are listed in the section 3.3. In section 3.4, the methodology and procedures adopted to choose the optimum VES are detailed. Section 3.5 describes the rheological characterization and it includes the methodologies adopted to study the effect of parameters on WLM growth in section 3.5.1,to compare the potential of VES and polymer as the mobility control agent in section 3.5.2, to study the effect of adding polymer to VES forming VES/P systems in section 3.5.3 ,to characterize the VES's potential in enhancing the EOR applicability in highly saline reservoirs on section 3.5.4, to characterize the viscoelasticity and to determine VES's potential in enhancing the EOR applicability in fractured reservoirs 3.5.5. Section 3.6 describes the methodology adopted in IFT characterization to study the effect of parameters such as concentration, temperature, aging, surfactant addition and polymer addition etc. Section 3.7 compiles the procedure adopted to quantify the viscosity/IFT ratio of VES, S/VES and VES/P systems in section 3.7.1, 3.7.2 and 3.7.3 respectively. The procedure for comparison of these systems is detailed on Section 3.7.4 and the most optimum one

among the studied systems is recommended for core flooding. Section 3.8 details the procedure involved in the viscosity measurements using Ostwald viscometer. Section 3.9 includes the procedures and methodologies adopted in quantifying the thermal stability of VES. Section 3.9.1 details the procedures adopted for measuring the thermal stability through thermo gravimetric analysis and section 3.9.2 details the methodology adopted for quantifying the long term thermal stability. IFT and rheological measurements are being used extensively. Section 3.9.3 outlines the methodology adopted to improve the thermal stability of VES. The sequential procedure adopted for measuring the residual oil saturation reduction capability of optimum VES through core flooding is detailed in section 3.10. Section 3.11 incorporates the approach undertaken to study the problems associated with the conventional EOR techniques in the thin viscous heavy oil reservoirs and the possible solutions provided by thermally stable VES.

Chapter 4 contains the results attained while screening for the best VES at the corresponding to carbonate reservoirs. The screening was done based on the visual observation, IFT reduction and viscosity generation and their results are presented in 4.1, 4.2 & 4.3 with discussion. The optimum one was chosen at the end and recommended for complete characterization.

Chapter 5 contains the results attained upon complete characterization of the optimum VES as an EOR fluid. In section 5.1, the results achieved through rheological characterization are presented. Under rheological characterization, several objectives were intended and their results are presented sequentially. The results attained while studying the effect of parameters on WLM growth are presented and discussed in detail in section 5.1.1. VES and polymer comparison results are presented in section 5.1.2.

Shear viscosities of VES upon adding polymer is presented in section 5.1.3 along with the discussion at the molecular level. Results associated with the rheological characterization for high salinity and fractured reservoirs are presented in sections 5.1.4 & 5.1.5. The results associated with the IFT characterization are presented and discussed throughout sections from 5.2.1 to 5.2.7. Viscosity/IFT ratio of VES, S/VES and VES/P systems are presented in sections 5.3.2, 5.3.3 and 5.3.4 and the comparison between them is presented in section 5.3.5. The optimum combination among the various systems was chosen and recommended for core flooding. Results and discussion associated with the thermal characterization of VES is presented in sections 5.4.1 (short term) and in 5.4.2 (long term) and in 5.4.3 (optimization). Section 5.4.4 summarizes the conversion of optimum VES from well stimulation fluid to EOR fluid upon thermal optimization and advocating it as an EOR fluid. Core flooding results with optimum VES is presented sequentially in section 5.5. The results associated with permeability measurements, connate water saturation estimation are presented in sections 5.5.1 and 5.5.2. Results attained while studying the effect of VES to reduce the residual/remaining oil saturation in water flooded core is presented in section 5.5.3. The potential of studied optimum VES and Wintershall's proprietary VES is compared in section 5.5.4. The potential of VES with other EOR methods is compared in section 5.5.5. The problems overlooked in core scale studies using the other EOR methods were elaborated and the recommendations are made to combat those using VES in section 7.2.

Chapter 6 contains the simulation results. It briefs about the novel dual mobility control concept in section 6.1. The sensitivity studies on steam flooding and polymer flooding is done by varying the thickness and oil viscosity and the results are presented in sections

6.2 and 6.3. Simulation results attained upon performing hybrid EOR operation by combining thermally stable VES with hot water are presented in section 6.4. The results obtained while performing sensitivity studies on the expected viscosity reduction of heavy oil due to the heating are presented in section 6.4.1. Section 6.4.2 compares the potential of VES/Hot water flooding with steam flooding, polymer flooding and hot water flooding in the thin viscous heavy oil reservoirs at the thickness of 20ft and oil viscosity of 3000 cP.

Chapter 7 includes conclusion and recommendation. Section 7.1 summarizes the outcome upon evaluating the potential of novel viscoelastic system as the chemical EOR method in carbonate reservoirs. Recommendations for future EOR studies with VES are made in section 7.2.

CHAPTER 2

LITERATURE REVIEW

2.1 Chemical EOR

A considerable portion of the current world oil production comes from the mature fields and the replacement rate of the produced reserves has been declining steadily over the last few decades. Consequently and fortunately for EOR researchers, the oil price keeps rising which make variety of expensive EOR processes a feasible one to recover the remaining reserves. The one main aim of any EOR technology is to increase the capillary number, so that the discontinuous residual oil could be mobilized and the relative permeability of oil could be improved on macroscopic scale. The entire EOR processes can be explained by Darcy law (Ali 2013). The other aim of EOR technologies is also to decrease the mobility ratio to avoid fingering, to facilitate better sweep efficiency. This is of concern to heavy oil reservoirs and highly heterogeneous reservoirs.

Chemical Enhanced Oil Recovery is attributed to reduce IFT , increase capillary number , enhancing microscopic displacement efficiency , improving mobility ratio and increasing macroscopic sweep efficiency (Sheng 2010).Chemical Enhanced Oil Recovery processes, in the words of (Lake 1989), "tantalized the industry with promises of significantly improved recovery and gained attention in 1980's. The aim of chemical EOR method is to increase the capillary number. Polymer flooding increases the capillary number by increasing the viscous force while surfactant flooding do so by reducing the Interfacial tension between oil and formation water/injection water. So the combination of surfactant

and polymer named as SP flooding combines the benefit of both. Multicomponent systems such as SP,ASP flooding are susceptible to chromatographic separation (Li, Shi et al. 2009; Lyons and Plisga 2011).

Generally, the chemical EOR method cannot be applied to deeper reservoir as the high temperature and salinity causes the degradation of chemicals. Miscible flooding had been applied for reservoir deeper than 9000 ft. Also chemical EOR cannot be applied to the heavy oil due to unfavorable mobility ratio between the injected fluid and heavy oil. Thermal methods are applicable in the reservoirs whose oil viscosity is above 150 cP. Also carbonate reservoirs are not the favorable candidates for chemical EOR mainly because of high salinity, temperature, low injectivity, fracture, low permeability etc. Most of the conventional surfactants and polymers are susceptible to high salinity, high temperature etc. The aim of this research is to evaluate the potential of VES as the potential EOR slug in carbonate reservoirs.

2.2 Variants of Chemical EOR

Among the chemical methods, polymer flooding has been applied largely. Some of successful polymer projects include Daqing Oil Field (China), Marmul field (Oman), North Burbank unit (USA), Sanand field (India). Polymer flooding has been widely applied to enhance oil recovery in China too (Wang, Dong et al. 2009). However polymer flooding can only be used to improve sweep efficiency with effective mobility control and viscoelasticity was not considered as the factor (Jennings, Rogers et al. 1971). Polymer flooding cannot contribute to displacement efficiency (Zhao 2001). Surfactant can be combined with polymer to do SP flooding (Green and Willhite 1998). The polymer makes the viscosity of displacing fluid closer to oil to achieve favorable mobility

ratio. Injecting surfactant alone causes the relative permeability of water to increase and it balanced by decreasing the aqueous mobility with polymer (Hirasaki and Pope 1974).The combined flooding process can increase both displacement efficiency and mobility control. Alkali and surfactant can also be added to the polymer to conduct ASP flooding. Alkali can react with minerals such as silicate minerals, alumina silicate minerals, and calcium and magnesium compounds to form scales (Katsanis, Krumrine et al. 1983). Scale formations and stabilized emulsions made people more interested in the technology of surfactant- polymer (Fu, Gao et al. 2004). Usually surfactant helps in reducing the IFT to ultra-low value up to 10^{-2} m$\frac{N}{m}$ thereby increasing the capillary number. As a result, very low residual oil saturation is achievable. Oil Industry has witnessed the use of surfactants for more than 80 years. Polycyclic sulfonate and wood sulfate were used as early in 1920's to improve oil recovery (Groote and Bernhard 1941).

The surfactants used in 1960's (Hirasaki, Miller et al. 2008) were made either by direct sulfonation of aromatic groups or by organic synthesis of alkyl/aryl sulfonate. In 1970s, an extensive research and field testing was triggered by the anticipated increase in oil price. It was recognized that capillary number controlled the amount of residual oil remaining after flooding by conducting extensive series of studies (Taber 1969; Melrose 1974; Stegemeier 1977). General revelation from these studies stated the reduction of IFT from 20-30 m$\frac{N}{m}$ to 0.001-0.01 m$\frac{N}{m}$ leads to the lowest residual oil saturation.

Four criteria for selecting the surfactant for tertiary EOR process were proposed much earlier (Gale and Sandvik 1973): (a) Low oil – water IFT, (b) Low adsorption, (c) Compatibility with reservoir fluids and (d) Low costs. Recently (Zhu, Zhang et al. 2013)

investigated the applicability of following methodologies to screen and design the surfactants capable of providing ultra-low IFT.

a. Hydrophilic- Lipophilic Balance (HLB) values,
b. R-ratio (ratio of interaction energy of surfactant and oil with surfactant with water in interface layer),
c. Molecule Geometry Packing Parameter (MGPP) and
d. Quantitative Structure- Property Relationship (QSPR).

Easy solution for mobility control through water soluble polymers mostly polyacrylamides was developed (Pye 1964). Since then, synthetic and bio polymer applicability along with other methods become popular in EOR technologies. But it was found that injecting polymer is not the best option always. It has limitation such as degradation, poor stability, compatibility, inability to access low pore volume, low injectivity. Susceptibility of the polymer to detrimental effect caused by high temperature and high salinity commonly found in reservoirs was noticed (Seright 1983). Carbonate reservoirs are usually characterized with high temperature and salinity. Inability to access low pore volume might preclude polymer applicability as an EOR fluid in low permeable carbonate reservoirs.

The following experiments were conducted by (Levitt and Pope 2008) to select the polymer : (a) Polymer hydration , (b) Filtration of Polymer and Surfactant compatibility, (d) Viscosity, (e) Chemical stability, (f) Degree of hydrolysis , (g) Calcium tolerance , h) thermal stability and (i) Core flooding

SP flooding provides lower residual oil saturation and lower mobility ratio. (Gao, Towler et al. 2010) evaluated surfactant polymer flooding potential and stated from industrial experience that following criteria should be met before developing SP flooding

a. The oil gravity is greater than 25 $°API$.
b. Oil saturation is greater than 30 % and light intermediates are desirable
c. Depth of the reservoir should be less than 8000 ft and reservoir temperature should not exceed 175 $°F$
d. Formation permeability greater than 20 mD and net thickness greater than 10 ft
e. Sandstone is preferred

2.3 Chemical EOR based on Formation

Most of the demonstrated chemical EOR applications were in sandstone reservoirs (Manrique, Thomas et al. 2010). Less than 20% of the chemical EOR projects were conducted in carbonate reservoirs, in which 64 polymer flooding projects and 6 SP projects were reported. Few case studies were reported in detail and most were listed in statistical reports. Earlier (Manrique, Muci et al. 2007) summarizes the EOR experience in carbonate reservoirs. He identified miscible gas injection is a feasible method in such low permeable reservoirs to overcome low injectivity. He found that chemical methods contribute marginally in terms of overall recovery. They realize that if the chemicals are stable enough at high temperature, high salinity and divalency, chemical EOR could significantly enhance the recovery in tight carbonate reservoirs. Viscoelastic Surfactant with excellent thermal stability and resistivity to salinity and divalency has recently been an option (Morvan, Degre et al. 2012). Although few cases of viscoelastic surfactant application has been tested for sandstone, carbonate reservoirs remains almost unstudied

for VES usage as an EOR fluid. Although no extensive field case studies for chemical EOR in carbonate reservoirs is available, it was demonstrated that carbonate reservoirs can be chemically flooded (Adams and Schievelbein 1987) Various kinds of surfactants(cationic, anionic , non-ionic and amphoteric) have been used for such an application in low permeable carbonates (Austad and Milter 1997; Hirasaki and Zhang 2004; Seethepalli, Adibhatla et al. 2004; Gupta, Mohan et al. 2009; Han, Fuseni et al. 2011; Yousef, Al-Saleh et al. 2011). These studies gave us a motivation that properly selected surfactants can recover additional oil in carbonate reservoirs. Natural fractures are more common in carbonate than in sandstone. High density of fractures and high permeability zones, low matrix permeability zone leads to the uncertainty of fluid flow in carbonate reservoirs. Presence of these fractures and diversified zones tend to complicate the EOR applications in carbonate reservoirs.

Carbonate reservoirs rocks are usually characterized by the low permeability matrix with high fractures (Ehrenberg and Nadeau 2005). Hence, injectivity becomes an imminent problem with any reasonable concentration of polymer in such carbonate reservoirs. Also carbonate reservoirs contains high concentration of divalent ions which hinder the applicability of conventional SP systems. SP systems are prone to chromatographic separation (Lyons and Plisga 2011). Most of the carbonate reservoirs are also characterized by high temperature and salinity. Surfactant alone cannot be applied without effective mobility control. Mobility control process is aided by injecting polymer. Particularly in Middle East, applicability of chemical EOR in carbonate reservoirs is complicated by high temperature and salinity (Han, AlSofi et al. 2013). At high temperature, the stability of chemicals particularly polymer gets affected. At high

temperature, the surfactant tends to precipitate upon exposure to divalent cations and will partion to the oil phase at high salinities. These carbonate reservoirs require specially formulated chemicals system which could mitigate the above problems. Employing Viscoelastic surfactant as an EOR fluid was sought to address these problems.

2.4 Viscoelastic Fluids Flooding

All non-Newtonian are Visco-elastic that they combine with both elastic and viscous properties. When the time scale of flow is much less than the relaxation time of the viscoelastic material, elastic effects dominate. It leads to the increased displacement efficiency. Extensive researches were conducted to test the high performance and low costs chemical systems. Previously in Polymer flooding, the viscoelasticity of polymer was ignored by many researchers (Smith 1970; Jennings, Rogers et al. 1971). A number of authors have presented laboratory results showing the effect of viscoelasticity on the displacement efficiency in polymer flooding operations. Elastic properties of the injected fluids using viscoelastic polymer was found to increase the displacement efficiency substantially while performing core flooding (Wang, Cheng et al. 2000). The effect of viscoelasticity of the polymer solution was also studied by (Wang, Wang et al. 2007), (Xia, Wang et al. 2008), (Jiang, Wu et al. 2008) who, in agreement with the previously mentioned studies, attributed the increase in oil recovery to elastic properties of the polymer solutions. Recent studies done also discuss the influences of viscoelasticity on the displacement efficiency (Wang, Xia et al. 2010). All the authors unanimously suggested that proven polymer flooding method using high concentration viscoelastic polymer solution could result in higher recovery when compared with water flooding and conventional polymer flooding. Attributed reason by them is the high elasticity of the

polymer solution, which resulted in increased displacement efficiency. (Urbissinova, Trivedi et al. 2010) studied the effect of elasticity alone during viscoelastic polymer flooding and reported that wider Molecular weight distribution of polymer solution increases the elastic properties which in provides the additional resistance for the polymer solution to flow through porous media and led to the higher oil recovery and lower residual oil saturation. They concluded that sweep efficiency of the polymer flooding operation could be enhanced by the optimizing or increasing the MWD of the polymer solution. More than 20% OOIP compared to the water flooding can be achieved by injecting higher concentration of polymer (Wang, Wang et al. 2011). However injecting such higher concentration possesses injectivity problems. Carbonate reservoirs rocks are usually characterized by the low permeability (Ehrenberg and Nadeau 2005). Hence, injectivity becomes a problem with high concentration of polymer in carbonate reservoirs. An additional increase of oil recovery (7-14% of OOIP) was reported after polymer flooding in Daqing Oil Field (Wang, Cheng et al. 2000).The displacement efficiency of the polymer injection was discussed from the perspectives of the capillary number and the viscoelasticity (Wu, Wang et al. 2007). (Xia, Wang et al. 2008) studied the mechanism of polymer solution from a microscopic perspective and found that large micro force during polymer flooding that resulted in the higher displacement efficiency. (Ranjbar, Rupp et al. 1992) quantified and optimized the viscoelastic effects of polymer solutions for Enhanced Oil Recovery and found that an index based on Maxwell-Fluid-Relation is used for quantifying the viscoelastic behavior of polymer solutions in porous media and not the usual relaxation time. They reported the existence of an injection rate beyond which viscoelasticity of the solutions is reflected by the increased effective

viscosity. The critical injection rate is dependent on the concentration and degree of hydrolization, molecular weight of polymers, core permeability, salinity and temperature. These parameters could be optimized to exploit viscoelastic nature of the solutions according to reservoir conditions. Reservoir condition changes drastically in reservoirs undergoing any EOR process. Following two methodologies were prescribed by (Dahanayake, Yang et al. 2004) to determine the existence of viscoelasticity of any liquid.

a. Swirling the solutions and visually observing the bubbles created by swirl recoild after the swirling is stopped.
b. during the frequency sweep test, the substance should possess the following
    1. G' should be higher than G" at some points below 10 $\frac{rad}{s}$
    2. G' should be at-least higher than 10^{-2} Pascal.

2.5 Viscoelasticity and Recovery Mechanism

For the same capillary number, displacement efficiency and recovery factor are comparatively higher if the viscoelastic fluid is used as the driving fluid rather than the Newtonian fluid (Wang, Xia et al. 2010). They studied the micro forces in pores causing the displacement efficiency during flooding. Two types of micro forces acting are first normal force caused by the change in the shape of the flow lines in pores and kinetic force caused by the change in the momentum which is due to the change in flow lines in pores. They concluded that flow lines in pores of viscoelastic fluid are different than flow line would be Newtonian fluids are important. Flow lines looks like expanding and contracting with viscoelastic fluids. Micro forces in pores are larger for viscoelastic fluids

than Newtonian fluids. Effect of micro forces on residual oil during chemical flooding was studied (Xia, Wang et al. 2008) . They conducted extensive experiments to study the influence of elastic characteristics of the driving fluid on displacement efficiency. They concluded micro forces are the main reason for recovery and it doesn't change the pressure gradient and it could act mainly on the protruding portion of residual oil to change the shape thereby mobilizing it. They interpreted that intense of micro forces acting on the residual oil increases with increased elasticity and it could result in increased displacement efficiency for viscoelastic displacing fluids at constant pressure gradients conditions. The displacement mechanism of polymer solution with visco elastic behavior was studied by (Wang, Xia et al. 2001) and it was concluded that higher the viscoelastic characteristic nature, higher the displacement efficiency. Flow characteristics of viscoelastic polymer using finite volume method in expansion channel , contraction channel and expansion contraction channel were studied by (Yin, Wang et al. 2012) and it was interpreted that the elasticity of the polymer solutions is proportional to the polymer velocity, the micro scale sweep efficiency and the flowing area and thus they interpreted that sweep efficiency could be improved. The new simulation model for viscoelastic polymer flooding was developed by incorporating the displacement efficiency due to the elastic nature along with viscous nature (Wang, Ye et al. 2013).

2.6 Injectivity Issues of Polymers

Injectivity is term used to describe the easiness with which the fluid can be injected into the formation. Exploiting the viscoelastic nature through injecting high concentration polymer may not be an ideal option for carbonate reservoirs characterized by low permeability. Injectivity becomes a severe issue. Poor injectivity may hamper the overall

efficiency of EOR process by causing loss of viscous force, delayed front movement, loss of reservoir energy etc. Surfactant possessing viscoelastic properties can be an alternative. Viscoelastic surfactant technology has been developed to match the rheological properties of the polymer solutions in a wide range of temperature and salinity without posing injectivity problems (Degre, Morvan et al. 2012). Carbonate reservoirs rocks are usually characterized by the low permeability matrix with high fractures (Ehrenberg and Nadeau 2005). In this research, we compared the potential of VES and polymer shear thinning nature, an indicative of their easy entry into perforated regions without causing injectivity problems. Apart from problems due injectivity problems and inability of polymer to get into low permeable region due to its rigid covalent backbone, the harsh conditions in carbonate preclude the applicability of conventional polymer as the mobility control agent. VES also provide the advantage of IFT reduction which the polymer cannot. Hence stable and flexible viscoelastic surfactant is sought as an option.

2.7 Viscoelastic Surfactant

Viscoelastic surfactants are the special class of surfactant that self assembles at favorable conditions forming wormlike micelles (WLM) generating huge amount of viscosity. It has the special property of relieving stresses (Chellamuthu and Rothstein 2008). This could address the problems associated with injecting high concentration polymer for exploiting viscoelastic recovery. Further VES performs much better at harsher conditions than at mild conditions (Degré, Morvan et al. 2011). The reasons are attributed to typical formation of WLM which is discussed in detail in this research.

Several classes that form wormlike micelles include classical cetyl trimethylammonium bromide – salicylic acid (Hoffmann, Rehage et al. 1982), Gemini amphipiles (Shrestha, Nomura et al. 2012), and Gemini quartenary ammonium systems (Knox 2011) Viscoelastic surfactants were also developed based on the betaine structures (Morvan, Moreau et al. 2009) and (Degré, Morvan et al. 2011). Cationic cetyl trimethyl ammonium bromide and cetyl pridium halides were used to formulate viscoelastic surfactant (Awang, Japper et al. 2012). Amphoteric alkyl amido betaine surfactant was also used(Berger and Berger 2008). Erucyl dimethyl amido propyl betaine (EDAB) was used as a VES in VES/P system (Zhu, Zhang et al. 2013). Viscoelastic surfactants based on Triphenoxymethanes (TPM) were developed (Brand, Hansch et al. 2014). It was reported that the TPM class of surfactants contains compact hydrophobic group and three long flexible hydrophilic tails. This was in contrary to the conventional viscoelastic surfactants which contain compact hydrophilic group and long, flexible hydrophobic group.

VES has been a successful well stimulation fluid. VES had been a part of successful field applications in low permeable rocks such as in Hydraulic fracturing (Boyer, Glenn et al. 2005), Foam (Semmelbeck, Deupree et al. 2006), diverting agents (Nasr-El-Din, Chesson et al. 2006). Experiences from these applications demonstrate the positive improvements of turbulent drag reduction, less formation damage, easier production rehabilitation coupled with the favorable flow and rheological properties. These properties encourage us to consider VES as an EOR fluid.

In this research, we are evaluating the potential of Akzonobel based stimulation fluids (viscoelastic surfactant) as an EOR fluid. Amphoteric surfactant called Amide Tallow-(3-dimethyl amino) propyl), N-oxide was screened as the best among the three surfactants

tested and considered as an EOR fluid in carbonate reservoirs. The screening was done at conditions encountered in carbonate reservoirs.

Surfactant having both hydrophobic and hydrophilic moieties on the same molecule has the tendency to self-assemble into variety of structures. The structures could be spherical, WLM or bilayer depending on several factors. Surfactant forms WLM, a characteristic of viscoelastic surfactant (VES) if it contains short hydrophilic head group and long hydrophobic tail groups. Precisely, the ability of the self-assembling surfactants to form WLM is based on packing parameter (Candau and Oda 2001). Packing parameter p is defined as:

$$p = \frac{v}{A \times l} \quad \text{..... (4)}$$

Where

- p is the packing parameter
- v is the effective hydrophobic chain volume
- A is the area per polar head
- l is the surfactant alkyl chain length

If p is less than 1/3, spherical micelles are likely to form. If p is in between 1/3 and ½, cylindrical micelles can be formed. If p is in between ½ and 1, then bilayer structures would be formed (Candau and Oda 2001). It is understood that A, the area of polar head has to be smaller for which the salts are added to screen the repulsion among the head groups (Chellamuthu and Rothstein 2008). This indeed facilitates its applicability for carbonate reservoirs containing high salinity. Further, the optimality has to be there between the parameter v and l, the parameters influencing the hydrophobic region. Hence

to have *p* between 1/3 and ½, it is essential to have surfactant hydrophobic tail length twice the volume of hydrophobic head. *A*, the area has to be smaller so that the head groups could be clustered together, for which the salts are essential to prevent electro static repulsion between them. Hence this is favorable for high saline reservoirs. At high concentration, these micelles can entangle each other (Chellamuthu and Rothstein 2008), like the entanglements of long synthetic polymers in concentrated solutions. These giant wormy micelles are also called as "living polymers" because their length distribution is not fixed by chemical synthesis but can vary reversibly in response to changes in the concentration, temperature and flow rate (Larson 1999). These behaviors of VES are unique and can be exploited. At favorable conditions, these aggregates can grow as long as few micrometers (Candau and Oda 2001). The favorable conditions are ascertained. It has been reported that the favorable conditions are more prevalent in carbonate formations. Carbonate formation with harsh conditions which restricts the applicability of conventional chemical EOR methods are indeed conducive for the applicability of the viscoelastic surfactant flooding. The positive response of WLM growth in VES with increasing salinity and temperature are beneficial. It is studied in this research.

A recent laboratory study reported 10% incremental production could be achieved by considering VES as mobility control agents (Lakatos, Toth et al. 2007). But their proposed surfactant mixture exhibited poor salt tolerance and its application was restricted to low salinity reservoirs. In this study, we are evaluating the potential of VES in high salinity carbonate reservoirs.

Using the proprietary betaine based viscosifying surfactant (Degré, Morvan et al. 2011), two types of core flooding experiments were performed with miniaturized clashach

sandstone cores. The permeability of the cores is between 1824 and 4992 mD. The core length is 5 cm and diameter is 1.3 cm. the salinity and temperature are 6300 ppm and 51℃. In the type 1, VES (0.3%) is injected after polymer (900 ppm) to see the incremental oil recovery compared to polymer flood. In type 2, VES (0.3%) is injected after water flooding to see the incremental oil recovery compared to water flooding. Type 1, gives the incremental oil recovery of 15%, regarding polymer. Type 2, gives the incremental recovery of 12%, regarding water flooding (Degré, Morvan et al. 2011). We are evaluating the potential of VES in tougher scenario in terms of formation nature, the carbonate. Salinity of above 210,000 ppm is way higher than the tested one and temperature of 80℃ is also in the higher range. The carbonate core, which will be used, is the low permeable core complicating the conditions further.

Wormlike micelles formed using cationic cetyl trimethyl ammonium bromide and cetyl pridium halides were tested as an EOR fluid in sandstone reservoirs. The salinity corresponds to 31,000 ppm and the temperature is 60℃. It has been reported that using 2.5 PV of WLM fluids could give an additional residual oil recovery of 16% (Awang, Japper et al. 2012). We are testing the VES potential at the much extreme conditions.

The usage of Viscoelastic surfactant for high saline reservoirs has been proposed (Morvan, Moreau et al. 2009) . It is the betaine based VES. Further the injectivity issue commonly associated while using high concentrated polymer to aid the displacement efficiency was mitigated by employing viscoelastic surfactant. However we are comparing the potential of VES and polymer shear thinning nature in highly saline conditions that corresponds to carbonate reservoirs. Apart from better injectivity index, shear thinning nature of injectant EOR slug also provides enhanced sweep efficiency

which is also discussed. Also we are evaluating the reversible shear thinning mechanisms of VES through shear studies. More recently, it was found that high viscoelasticity of SP flooding is an important factor contributing to the higher recovery (Zhu, Zhang et al. 2013). We are evaluating the viscoelasticity of VES through dynamic studies with 57000 ppm saline water.

Viscoelastic surfactant has been studied as the mobility control agent in Low tension surfactant floods (Lakatos, Toth et al. 2007). The viscoelastic surfactant influenced the IFT at the lowest concentration thus the calculated CMC corresponds to 0.00497 g/L making this value as the smallest for the EOR chemicals. The positive effect due to it is that formation of worm like micelles starts at very low concentration contrarily smaller CMC does not mean effective solubilization as in the case of conventional surfactants. Viscoelastic surfactant influences the IFT at the lowest concentration but the IFT lowering is not sufficient to mobilize the residual oil after water flooding. Joint application of mobility control with highly efficient surfactant could increase the recovery up to 15-17%. In this research, we are formulating four different S/VES system to test its potential for complex carbonate reservoirs. it include Cat/VES, Ant/VES, Non/VES and Zwit/VES.

Surfactant and viscoelastic polymer systems (S/VEP) formulated by surfactant and viscoelastic polymer was studied for sandstone reservoirs (Wu, Wang et al. 2007). It emphasizes the importance of viscoelasticity in higher oil recovery. An interesting point they have concluded is even with higher IFT, displacement efficiency could be more due to the elastic nature. This motivated us to go ahead with VES systems that are not renowned for providing ultra-low IFT.

Further recently, (Zhu, Zhang et al. 2013) studied the main factors on oil recovery of Surfactant-Polymer flooding. They concluded that if the ratio of viscosity of the displacement fluid to that oil was more than 2, then the higher recovery could be obtained. Additionally they found that more than 15% of oil recovery is achievable if the IFT lowering is also considered along with the mobility control. However, using VES as a single fluid would be much better as there is the possibility of chromatographic separation (Li, Shi et al. 2009). In this research, we are considering VES as a single fluid as well.

The viscosity of betaine based viscoelastic surfactants at low concentration (0.1% to 0.5%) were measured (Degré, Morvan et al. 2011) and it was reported that the system is salt tolerant with the positive impact of brine concentration on viscosity. Thermal stability of Viscofying surfactants was studied at both 51℃ and 90℃. No viscosity loss was observed for 51℃ and a maximum of just 10% viscosity loss has been reported at 90℃. The study implied the better performance shown by VES over the conventional polymer whose hydrolysis exceeds 90% after 100 days. Even 70% hydrolysis may affect tolerability of calcium ions concentration exceeding 5,000 ppm (Levitt and Pope 2008). But carbonate reservoirs usually contains high divalent ions. Calcium tolerance is improved for sulfonated polymers having comparable degree of hydrolysis than regular HPAM but cloudiness could occur if calcium content exceeds 2,000 ppm. Turbidity associated with them was reported (Zaitoun and Potie 1983) and it was stated that it may lead to plugging behavior thereby making it difficult to use the polymers in those conditions. All these properties encourages us to test the potential of the optimum VES that could suffice in these conditions. However, we are testing the potential of VES/R

system's potential to improve the macroscopic driving force and to reduce the microscopic capillary force with the improved thermal stability. VES/R system is formulated for the stimulation based viscoelastic surfactant, not renounced for long term stability. So an optimization of thermal stability is done and reported. We are also considering carbonate core as the formation for VES EOR for which no literatures exist except (Dahanayake, Chabert et al. 2011). That too, none of core flooding results was reported. Even the bulk solution studies were done at the easiest operating conditions of 25℃ and the salinity of 2,400 ppm which is not the characteristic of most of the Middle East carbonate reservoirs.

The core flooding tests using VES/P, P and VES systems simulating conditions encountered at shengli oil field, china were reported (Zhu, Zhang et al. 2013). The conditions include the temperature of 85℃ , the salinity of 32,868 ppm and the divalency of 873 ppm. VES/P system comprises of Hydrolyzed polyacrylamide (HPAM) and Erucyl dimethyl amidoproplyl betaine (EDAB). With 0.3 PV of injection, ultimate recoveries for the systems were P ~15.8%, VES ~1.90% and VES/P ~ 10.2. Although P system gives higher recovery, its long term thermal stability is poor. Initial Viscosity of 18 cP of P system dropped down drastically to 4.88 cP after 3 days aging. Considering EOR fluid's longer residential time in reservoir, long term stability is crucial. Hence VES system is preferred whose long term thermal stability is consistently stable for 66 days. However, WLM breaks upon seeing oil (Berger and Berger 2008), thus giving the lower ultimate recovery. Hence considering the optimality between recovery factor and long term stability, VES/P hybrid systems is found to be the better one than VES and P systems. Polymer provides residual viscosity which is unaffected by oil thus improving

the recovery factor over VES system. VES forms WLM whose entanglement prevent/mitigate the degradation associated with P system. We are evaluating the VES potential in carbonate reservoirs with lower permeability. VES/P, VES and S/VES were also studied for its recovery potential in terms of viscosity/IFT ratio at conditions corresponding to the carbonate reservoirs.

Recently in SP flooding, it was found that usage of viscoelastic surfactant in the form of amphoteric surfactant along with polymer polyacrylamides could provide effective mobility ratio. (Wu, Huang et al. 2013) reported that injected amphoteric surfactant increases the viscosity of polymer there by making it an ideal combination to push the heavy oil with effective mobility ratio. They also reported that SP system they formulated for western Canadian heavy oil reservoirs exhibited good resistance to hardness (13,600 mg/L). In this research, we are analyzing the behavior and reporting the reason for the synergistic effect of adding polymer to VES.

The usual standard industry criterion claims that polymer flooding is not applicable for oil with viscosities more than 150 cP (Taber, Martin et al. 1997). Using VES, we are proposing a novel concept of dual mobility control for exploiting complex heavy oil reservoirs. We are targeting the thin viscous heavy oil reservoirs by formulating a hybrid EOR method employing VES/hot water. Its Comparative studies were carried out between steam flooding, polymer flooding, and hot water flooding, VES/hot water flooding for thin viscous heavy oil reservoir using the commercial reservoir engineering simulator.

The challenges to chemical EOR in high temperature, high salinity, low permeable carbonates was somewhat addressed (Levitt, Klimenko et al. 2013) . They stressed the importance of low permeable formation which requires optimized polymer molecular weight distribution in order to achieve better mobility reduction and injectivity. They concluded that for low permeable carbonate reservoirs (10-100 mD), optimized injectivity and viscofying power of polymer could be obtained by degrading a medium-MW copolymer. They found through viscosity measurements that degraded moderate – MW copolymer maintained a higher average MW than low-MW copolymer. We are optimizing through a living polymer which is VES that could undergo shear thinning and explore tight portion of the reservoir rock. It could be an effective replacement to polymer because using polymer as a lone single slug could not displace the oil. Microscopic displacement is very crucial in tight carbonate reservoirs. Adding surfactant to polymer may improve the displacement efficiency; however, there is possibility of chromatographic separation with the injection of multiple slugs (Lyons and Plisga 2011).

To increase the capillary number, injecting surfactant or polymer alone individually does not suffice (Dahanayake, Derian et al. 2008). Also the conventional SP flooding was expensive and possesses limitation in terms of compatibility, formation damage etc. So they claimed that viscoelastic surfactant capable of providing both displacement and sweep efficiency was considered as the single flooding fluid. They formulated the single flooding fluid with 1% of non-polymeric viscoelastic surfactant in water with salinity of 20 pounds/ 1000 gallons. They were able to achieve IFT of less than 1 milli Newton per meter (mN/m) and viscosity of about 10 cP. They selected the viscoelastic surfactant from the group of cationic, amphoteric, zwitterionic, and anionic or the combination of

all. The non-polymeric viscoelastic surfactant(s) they used were viscoelastic even at 350 °F and higher salinity. They also reported that non-polymeric surfactants that form viscosifying fluids are advantageous because they are of low molecular weight than polymers. They promptly reported that the extent of viscosity increase will vary depending on the surfactant type, brine content in the flooding fluid and in the formation, composition of oil etc. They reported that generation of viscosity up to 1000 cP through VES is possible. Another advantage of viscoelastic surfactant is that they remain stable in high shear applications. Also fluids containing VES have conductivity in the reservoirs. They suggested that non-viscoelastic surfactant can be added to the VES to enhance better IFT reduction and mobility control and for doing so; they reported that concentration of non-viscoelastic surfactant could be as low as 0.1%. Based on this, we are investigating the behavior of optimum VES, S/VES and VES/P systems by replicating the conditions encountered in carbonate reservoirs. All the relevant tests necessary for characterizing the potential of EOR fluid were carried out.

Applicability of VES to carbonate reservoirs was initially suggested (Dahanayake, Chabert et al. 2011). They proposed that VES could effectively plug the high permeable fracture and then VES could permeate in to high porous matrix. The viscous gel compatiblizes with the oil entrapped. They claimed that aqueous gel with VES should be injected into the reservoir for three to five days. Then the residence time of few days could be allotted and then production could happen for 10 days. They analyzed that they can inject the fluid at the low shear rate, but still it could generate huge viscosity within the reservoir upon the relaxation of shear. They also reported that polymer could be added to enhance the sweep efficiency of VES and surfactant could be added to enhance

IFT reduction. Although, it has been stated, none of the results were published. Even the bulk solution studies were done at the easiest operating conditions of 25℃ and the salinity of 2,400 ppm which is not the characteristic of most of the Middle East reservoirs. We are addressing it through rheological analysis. That is property needed for blocking the high permeable zone and entering the matrix zones are ascertained in our work. In this research, we are evaluating the potential of VES that has been originally designed for stimulation purpose. We are ascertaining all the basic and unique properties through various approached mentioned in the methodology.

Triphenoxymethanes (TPM) exhibiting viscoelastic natures have been under intense development since 2010 (Brand, Hansch et al. 2014). Core flooding experiments carried out with 2 D sandstone core at 55℃ and salinity of 186 g/L. based on the average of 6 experiments, it was found that 1 PV of 0.23% TPM injection gives the additional recovery of 14% and additional 10% recovery is achieved when flooded to residual oil saturation when compared with injecting saline water solution alone. In oil saturated core that has been flooded with saline water to residual oil saturation, injecting 0.23% of TPM in saline water mobilized 7% (OOIP) of residual oil. In spite of not providing ultra-low IFT, additional displacement and recovery is achieved. TPM's viscoelastic nature coupled with its shear thinning capability is perceived to be the main reasons (Brand, Hansch et al. 2014). In this research, we are dealing with much lower permeable carbonate core coupled with the higher salinity and temperature. A comparison between the TPM and optimum VES used in this research is provided.

2.8 Can VES expand Chemical EOR Applicability in Carbonate Reservoirs?

VES need harsh conditions to perform and carbonate reservoir are characterized by harsh conditions. Carbonate reservoirs are complex and characterized by high salinity, high temperature, low permeability and extensive fractures (Han, AlSofi et al. 2013), (Ehrenberg and Nadeau 2005). Just 20% of the total chemical EOR projects were conducted in carbonate reservoirs (Manrique, Muci et al. 2007). In SP flooding, the surfactant provides IFT reduction and polymer provides the viscosity (Green and Willhite 1998). IFT reduction is essential to reduce the residual oil saturation and viscosity is needed to increase sweep efficiency. High salinity causes the precipitation of surfactant and high temperature affects the stability of polymers. Viscoelastic surfactant is a stable chemical that could combat the harsh conditions and in fact need those harsh conditions to function at its best. It provides the dual function of IFT reduction and viscosity at harsher conditions. VES is a living polymer which forms Wormlike Micelles (WLM). WLM can grow up to few micrometers (Candau and Oda 2001) and it is sensitive to temperature, salinity, rate, concentration etc. The rheological aspect of VES as an EOR fluid was assessed (Sultan, Azad et al.2014). Carbonate reservoirs being characterized by high salinity, high temperatures could be an ideal candidate for facilitating the WLM growth. The chemical EOR formulation extensively for the carbonate reservoirs based on compatibility with sea-water, IFT, Viscosity, adsorption was developed (Han, AlSofi et al. 2013). Total recovery in EOR is the product of microscopic displacement efficiency and macroscopic volumetric sweep efficiency. The extensive presence of fractures in the carbonate reservoirs could lead to the drastic reduction in sweep efficiency. The injected

slugs tend to travel through the least resistant high permeable fractures without contacting/sweeping the oil in low permeable matrix. Fractures have to be blocked to facilitate injection fluid entry into low permeable zone. VES has been used in the oil industry for well stimulation process (Gomaa, Cutler et al. 2012). The ability of VES to break upon entering the high oil saturated zone coupled with its ability to remain viscous while entering the oil-free zone (water zone) is reported to be an ideal scenario for preventing entry of subsequent injected fluids into oil free zones (Nasr-El-Din, Chesson et al. 2006). Thus viscosifying VES could block and divert the subsequent slugs towards oil rich zone (Chang, Qu et al. 2001). This phenomenon can be exploited to block the fractures during EOR process. High concentration of VES can be injected initially to block the fractures. EOR is a full field process while stimulation is well bore process. So considering the economics, the low concentration of VES is preferred as the subsequent second slug for injection while targeting the less permeable oil rich zone. VES exhibits reversible shear thinning nature. This might facilitates the easy entry of viscous fluids into tight matrix.

VES breaks while contacting the oil (Berger and Berger 2008). Hence released oil could break the plugged VES. Viscoelasticity is the main property that contributes to sweep efficiency (Yin, Wang et al. 2006). The storage modulus (G') and loss modulus (G") of VES determines its ability to be a potential diverting agent. VES 3% is tested for and G' and G" at the angular frequency of 5 $\frac{rad}{s}$. Having blocked the high permeable region, the injected slugs have to enter the low permeable portion of the reservoir to displace the oil from it. The entry part of low permeable rocks exerts extra stress on the fluid. The shear thinning response of the fluids to the extra stress is vital for facilitating its entry towards

the low permeable region (Azad and Sultan 2014). Oil released from the matrix and low permeable region has to find a way towards the production well. The plugged VES acting as a diverting agent has to break to let the conduit. VES may break upon seeing oil (Berger and Berger 2008). Poorly stable VES at high temperature may also break by itself providing the path for the mobilized oil towards production well.

2.9 VES for Complex Heavy Oil Reservoirs

Heavy oil reservoirs account for more than 8 trillion barrels (Alboudwarej 2006). Thermal EOR methods such as steam flooding have employed to exploit heavy oil reserves. Screening criteria proposed by (Taber, Martin et al. 1997) limits the applicability of steam flooding to reservoirs with thickness above 20ft, sandstone reservoirs, and shallower reservoir not deeper than 4500ft. The problems restricting the applicability of steam flooding in thin heavy oil reservoirs are heat losses to under burden and over burden (Dyer, Huang et al. 1992). More than 80% of western Canadian heavy oil reservoirs accounting for 1.3 trillion barrels have thickness of less than 16 ft (Adams 1982). Even non-thermal method such as Polymer flooding would not be effective to displace oil with viscosity of more than 1500 cP. Hence both steam flooding and polymer flooding are not the preferred methods for thin viscous heavy oil reservoirs (Azad, Sultan et al. 2014). Exploiting the thermal stability of VES could be an option to formulate VES/Hot water flooding, the hybrid EOR method. The hybrid EOR method could provide dual mobility synergistically.

CHAPTER 3

METHODOLOGY

3.1 Overview of the Approach

In this research, the initial objective of choosing the optimum VES among the three surfactants was done with the aid of rheometer and IFT tensiometer based on viscosity/IFT ratio. Having chosen the optimum VES, the ability of it to improve the macroscopic sweep efficiency and microscopic displacement efficiency in a cost effective manner was determined. Further two more systems namely S/VES and VES/P systems were formulated. Five different concentration of optimum VES was used. Four different class of surfactant namely cationic, anionic, non-ionic and zwitterionic surfactant were combined with VES to form four different S/VES systems. Different combinations of VES and polymer were formulated to form VES/P systems. VES, S/VES and VES/P systems are studied for its viscosity/IFT ratio through the help of rheometer and IFT tensiometer. The shear rate of 5/s, salinity of 57,000 ppm and the temperature of 70℃ were used in these studies.

The detailed rheological characterization was done to

- Study the effect of parameters on WLM growth
- compare the potential of VES and polymer as a mobility control agent
- to study the effect of adding polymer to VES

- to characterize the elasticity and to investigate its potential to expand chemical EOR application in fractured carbonate reservoirs
- to characterize the impact of formation water and to investigate its potential to expand chemical EOR applicability in highly saline reservoirs

After characterizing the rheology, IFT characterization of optimum VES was done to

- to study the effect of concentration on optimum VES
- to study the effect of temperature on optimum VES
- to study the effect of adding surfactant to optimum VES
- to study the effect of adding polymer to optimum VES
- to study the effect of temperature on VES and S/VES
- to study the effect of aging on optimum VES
- to study the effect of reducing agent to optimum VES while aging

Having measured the shear viscosity and IFT of the VES, S/VES and VES/P systems and considering viscosity/IFT ratio at 70℃ as the yardstick, the optimum combination was chosen from it and recommended for core flooding.

Thermal stability tests were carried on VES and VES/P to determine the long term stability. Aging temperature include 65℃, 85℃ and 95℃. Thermal set ups, Thermo gravimetric analysis, oven, rheometer, viscometer and IFT tensiometer were the equipment used. Reducing agent was added to VES to test its potential in enhancing the thermal stability.

Viscoelastic systems are known for reducing the residual oil saturation drastically with lower usage. The optimum system's capability to reduce the residual oil saturation was measured through core flooding at the temperature of 80℃ and salinity of 210,000 ppm. The low permeable carbonate core of 113 milli Darcy was used. Various factors causing the excellent mobilization are mentioned. All the results are summarized to ascertain the possible extension of chemical EOR to carbonate reservoirs.

The simulation studies were done to study the effect of thickness and oil viscosity on steam flooding and polymer flooding for heavy oil reservoirs. Also it was done to compare the performance of steam flooding, polymer flooding and thermally stable VES/hot water flooding in thin viscous heavy oil reservoirs.

3.2 Equipment and Materials

3.2.1 Equipment

Rheometer, IFT tensiometer, thermo gravimetric analysis, viscometer, thermal set up, oven, core flooding apparatus were the main equipment used in this research. ECLIPSE, the commercial reservoir engineering software was used for simulation studies. The descriptions of that equipment are as follows:

Rheometer

It is used to measure the rheological properties that are crucial for macroscopic displacement efficiency. It includes the shear viscosity, elasticity, shear thinning etc. The **Figure 4** depicts the various parts of the rheometer. The body of the rheometer is rigid, single-piece metal casting comprising a base and column.

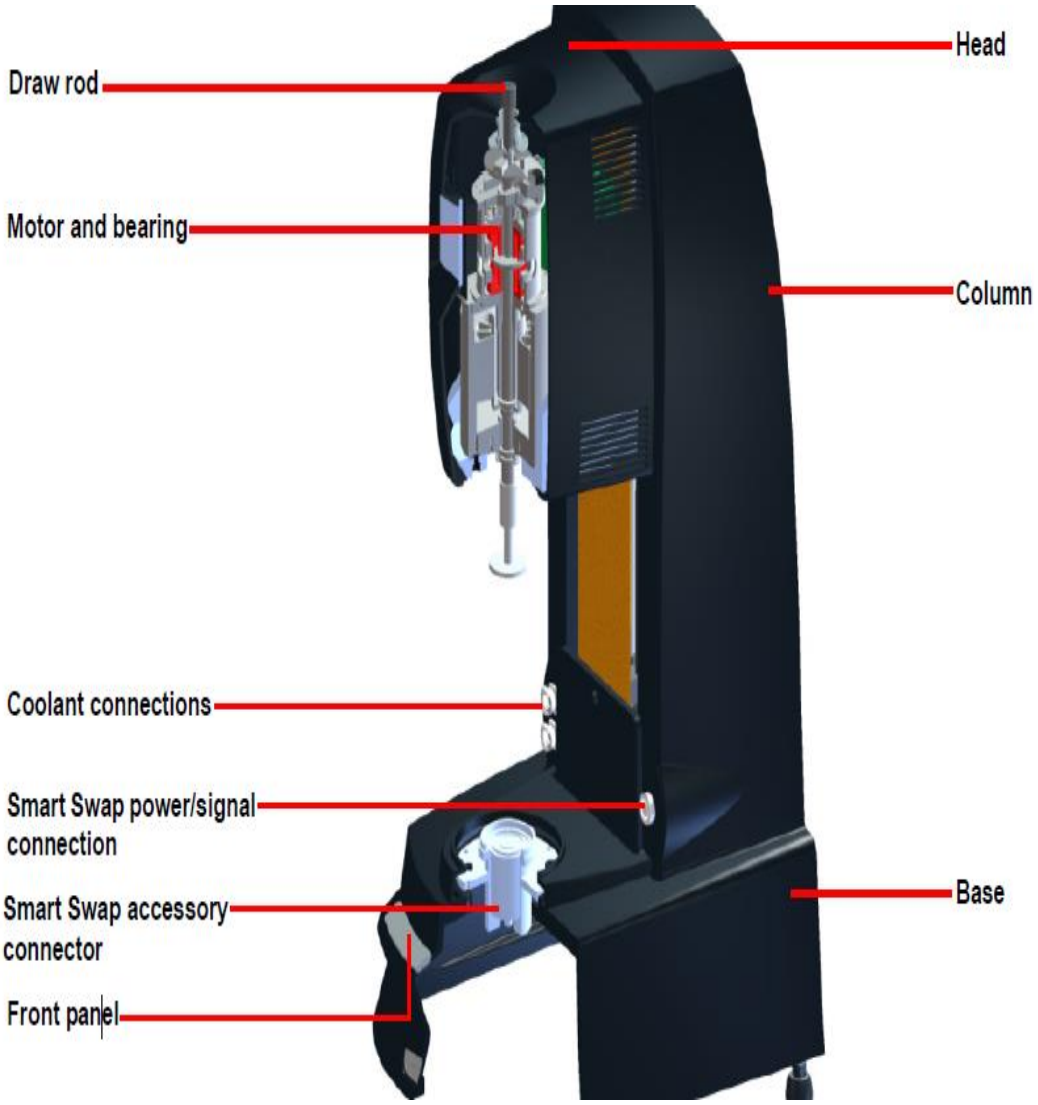


Figure 4: Schematic depicting the parts of TA rheometer

The instrument head is attached to a ball-slide, which is mounted within the column. The vertical position of the head is controlled by driving the screw of the ball-slide. The head contains the following:

- The drag cup motor, with an armature that forms the rotating spindle of the rheometer
- A magnetic thrust bearing that supports the drive shaft and two radial air bearings that align it.
- An optical encoder that determines its angular position.

Key rheometer components: The main components of the rheometer are

a. Casting: the body of the rheometer is single-piece aluminum, consisting of a base and column. The casting is an important component of the rheometer, as it needs to be rigid to axial and torsional stresses, robust and capable of being machined to high precision and accuracy to ensure correct alignment of the other components of the instrument.

b. Ball slide: The instrument head assembly containing the motor, bearing and optical encoder is mounted on a stiff, linear motion, precision ball slide guide. The ball slide is mounted with in the instrument column.

c. Magnetically- Levitated bearing: This bearing is important that controls the quality of data that can be obtained on the instrument. The design of the bearing involves several properties such as friction, stiffness, air consumption and toleration to misuse. In the Discovery Series rheometers, the thrust disc is retained, but it is levitated magnetically. The thrust disc is constructed from a magnetically susceptible material. Electromagnetic actuators are positioned above

and below the disc, the strength of the magnetic field generated by each actuator is controlled through the current supplied to its coils. The stronger the field, the greater the attraction between the actuator and the thrust disc. The axial position and motion of the spindle are detected by sensors mounted above the upper actuator, and can be closely controlled by varying the supplied current of each actuator coil. This arrangement has advantages over the traditional air-bearing in many aspects. The gap between the thrust disc and the stationary components of the instrument can be much wider, of the order of millimeters rather than micrometers. This results in both the friction of the bearing being substantially lower, and increases the smoothness of the rotation.

d. Radial air bearings: it provides stiffness in the radial direction. The discovery series rheometers are designed with two porous carbon radial bearings, located above and below the motor.

e. Motor: this rheometer uses the non-contact drag cup motor. A thin walled metal cup is mounted on the rotating spindle of the rheometer. A magnetic field rotating at 1000's of rpm is generated by continuously varying the current supplied to stationary pole pieces surrounding the cup. This produces an eddy current in the cup, which generates a second magnetic field. The two fields oppose each other , in accordance with lenz's law and the cup field is forced to follow the rotating field. Hence the cup is dragged round by the rotating field and a torque is generated whether the cup moves or not.

f. Front panel: Certain operations of the rheometer can be controlled through buttons on the front panel

Tests with rheometer: The following tests can be carried out with the rheometer. Concentric cylinder is used throughout the research. 22.5 ml of solution has to be injected in the concentric cylinder.

Table 1: Rheological parameters and its EOR application

Parameters	Application	Related tests
Shear Viscosity	Mobility control	Flow sweep, temperature ramp, time sweep
Elasticity	Blocking the fractures, Improving the sweep efficiency, Viscoelastic recovery	oscillation frequency, oscillation Amplitude
Reversible shear thinning	Entry to tight portion of the reservoir rock, avoiding injectivity issues, mobility control	Flow sweep

Interfacial tensiometer

It is used to measure the Interfacial tension between oil and the solution. The solution containing the surfactant lowers the IFT, thus mobilizing the oil and leading to its displacement. This tool is used to characterize the interfacial tension, the term in denominator of the capillary number equation. The **Figure 5** depicts the parts of the spinning drop Tensiometer from Kruss site 100. As it seen from the **Figure 6**, there exists a capillary tube system that is rotatable by adjusting the rotating speed regulator. Calibration is to be done using lens to get the focus range of the desired solution. Inlet and outlet for the fluid movement is clearly depicted. As the oil and surfactant solutions are injected, speed has to be adjusted by turning the speed regulator. Camera captures the

image of the oil droplet and it has to be adjusted in such a way that the movement of oil drop is captured. Illumination can be adjusted using the illuminator.

Measuring principle:

When a heavy bulk phase and a light drop phase are situated in the rotating capillary **(Figure 6),** the drop radius perpendicular to the axis of rotation depends on the interfacial tension between the phases (γ) , the angular frequency of rotation (ω) and the density differences between the two phases ($\rho_H - \rho_L$). For a given capillary, rotating speed and with known densities of the two phases, the interfacial tension between them can be calculated from the measured drop diameter d (=2r). At the same time, the length of the drop L along the axis of rotation must be at least 4 times the drop diameter (L≥ 4d) (Weser 2012).

$$\gamma = \frac{r^3 * \omega^2 (\rho_H - \rho_L)}{4} \quad \ldots\ldots\ldots\

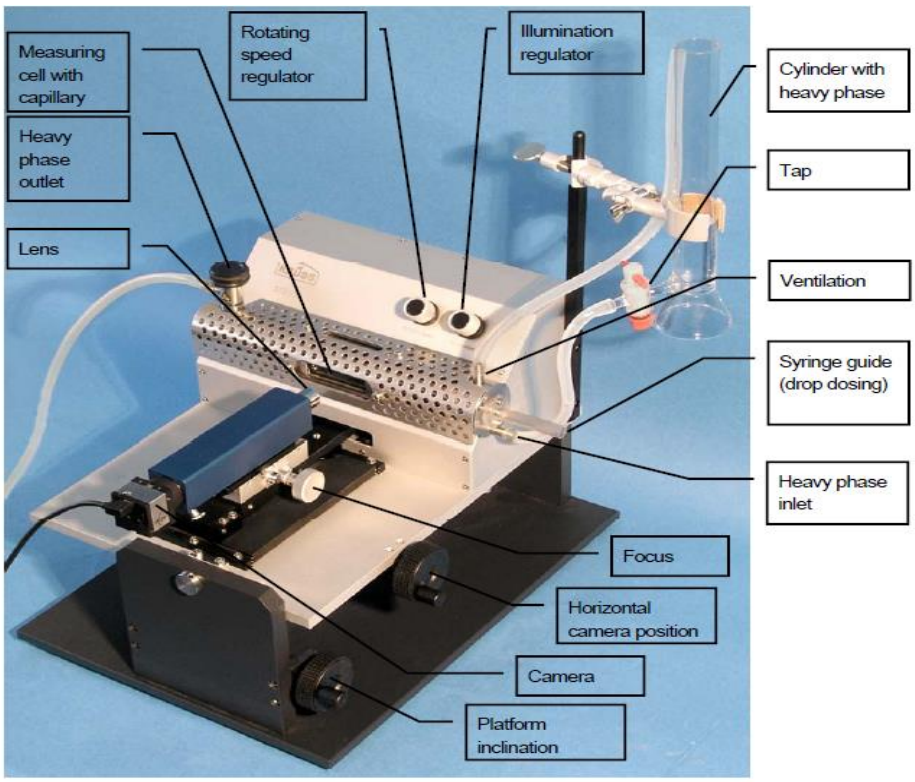


Figure 5: Schematic of Kruss Interfacial tensiometer

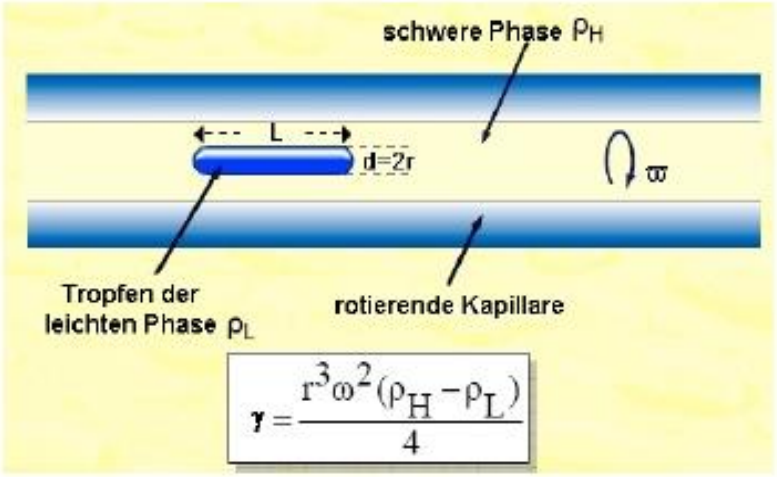


Figure 6: Schematic of capillary tube in Interfacial tensiometer

Ostwald Viscometer & Pycnometer

Viscometer and densometer are the equipment used for characterizing the fluid's ability to provide mobility control in EOR operations. Viscometer is used to measure the shear-free viscosity of the solution. Densometer is used to measure the density of the sample.

Ostwald viscometer is used to measure the viscosity of the solutions by noting the time taken by fluid to pass the prescribed distance. The **Figure 7** depicts the schematic of Ostwald viscometer. It has a thin tube on the right side and thicker tube on the left side. There are two markings in the thin tube for estimating the time taken by fluid while flowing through it. Upper marking shown in the **Figure 7** is where the time should be counted until it reaches the lower mark shown. Initially, fluid has to be injected through the thicker tubing on the right side until the fluid reaches the half way of the circular bulge. Lower ranges of size are meant for low viscosity substance. Smaller size has smaller opening and hence the low viscous substance that normally flow easily would require time and that time could be captured and substituted in the equation used for calculating viscosity. Viscometer with larger ranges induces the sudden flow of the less viscous fluid and the time captured for the flow would not really be giving the viscosity in correct ranges. However for high viscous substance, viscometer with larger opening is preferred than smaller opening to account for the lengthy time encountered while flowing the substance possessing higher resistivity.

The **Figure 8** depicts the schematic of pycnometer. The total volume of it is 10 ml and the density of the samples can be measured by finding mass of the sample and dividing it by the 10ml, the volume. The mass of sample is the difference between empty densometer and sample filled densometer.

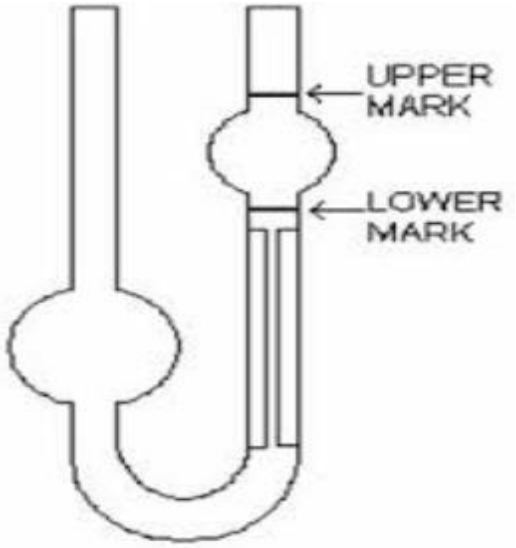


Figure 7: Schematic of Ostwald Viscometer

Figure 8: Schematic of 10 ml Pycnometer

Thermo Gravimetric analysis

The **Figure 9** depicts the schematic of TA Thermo gravimetric Analysis (TGA) instrument. It quantifies sample-mass discrepancy against temperature variations by making instantaneous weighting of the sample subjected that are subjected persistent heating in the controlled flow of air. The thermo-dependent process such as desorption, absorption, vaporization and decomposition that results is mass-loss can be monitored by TGA. TGA tracks the thermal stability and decomposition materials under the testing conditions of temperature and time by evaluating the compositional analysis on the sample upon coupling it with mass spectrometry.

Generally, three steps are involved while measuring the thermal stability of VES. They include

1. Desolvation (Evaporation): Loss of various ions of salts used while preparing the VES solution
2. Dehydration: Loss of bound hydrates and water
3. Decomposition: chemical and thermal stability

Thermal set-ups

The **Figures 10 and 11** depicts the set up designed for measuring the long term thermal stability. The **Figure 10** shows the front view of the set-up. It includes the series of thermal bath connected to condenser which in turn is connected to pipe designed to carry the nitrogen for creating the nitrogen atmosphere in the set-up. Vacuum pump is also used to create vacuum after removing the samples from the set-up. Both vacuum pump and nitrogen cylinder are displayed in the **Figure 11.**

Figure 9: Schematic of TA Thermo Gravimetric Analysis

Figure 10: Front view of Thermal Stability set up

Figure 11: Side view of Thermal set up with nitrogen cylinder & vacuum pump

Oven

The **Figure 12** depicts the oven used for monitoring the long term thermal stability of VES solutions at 95℃. The temperature of the oven is set at 95℃ by adjusting the knob. The corresponding temperature is monitored through thermometer placed above the oven. Knob adjustment is done until the temperature remains at 95℃ in the thermometer. After setting the aging temperature, the samples were put in the voil, tightly closed and kept inside the oven for heating it.

Core Flooding Apparatus

The **Figure 13** depicts the interior view of core flooding apparatus. It includes the core holder where the sample core would be placed. Core holder is fixed at the right side and could be varied at the left side. A temperature sensor is located on the core holder. Several manually controllable valves are located inside the oven. These valves should be operated carefully. Two pistons are located inside the oven. Two pistons are located outside the oven as shown in the **Figure 14**. Computers and its control are located on the right side of the set up as shown in the **Figure 14.** Qx-8000 pump is on the right side of the pistons. Pump supply for Qx-8000 and fractional collector for collecting the effluents are located on the desk table. Transducer with BYPASS and INLINE manual valves are located on the top side.

Figure 12: Oven used for aging the samples at 95℃.

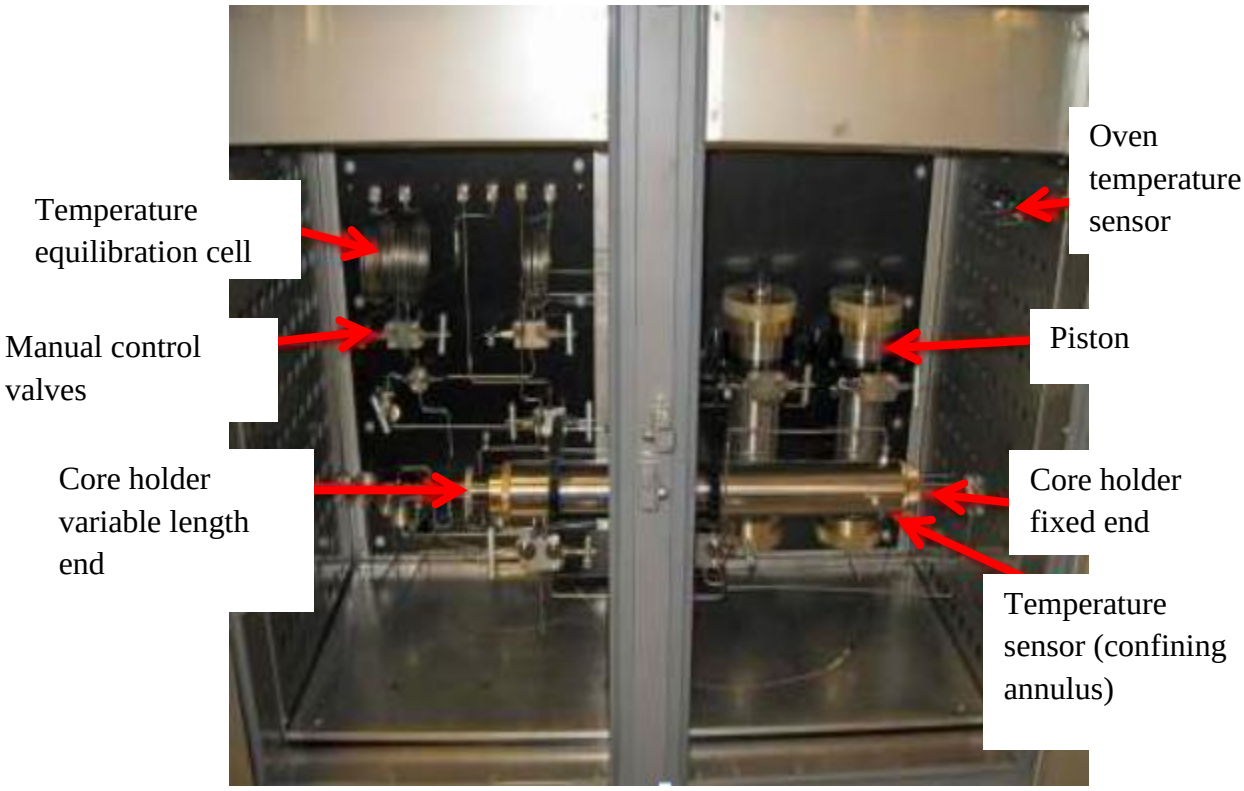


Figure 13: Front view of core flooding apparatus

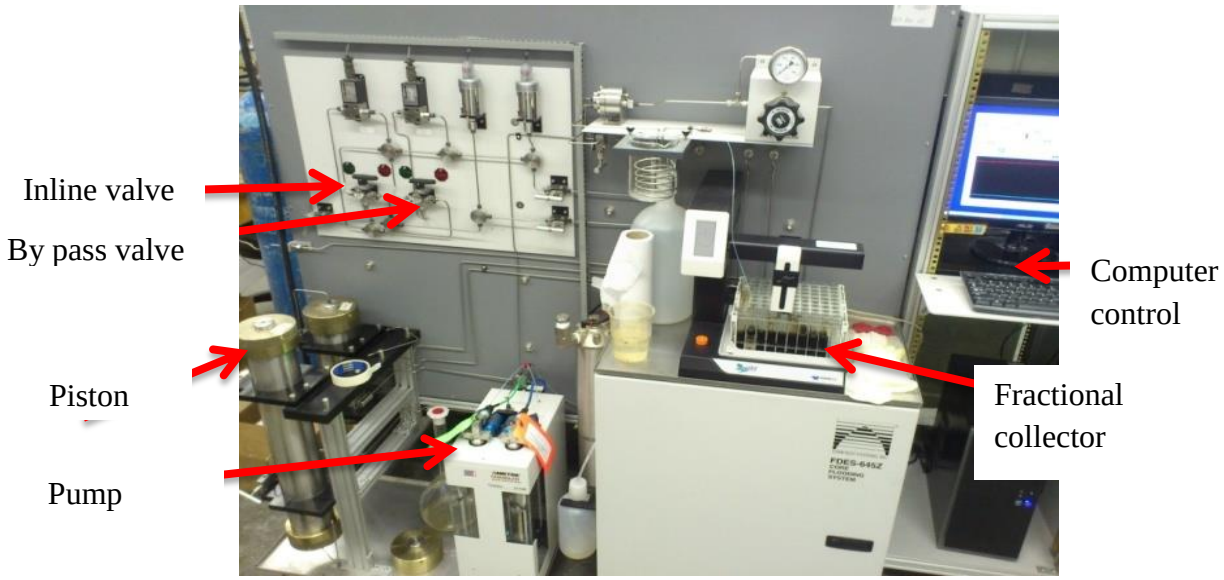


Figure 14: Back view of core flooding apparatus

Simulation Software

The ECLIPSE simulation software, the proprietary SLB software is used for simulation works involved in this research. Simulation studies are done on the basis of dual mobility control concept. Steam flooding is simulated with ECLIPSE 300 and polymer flooding is simulated with ECLIPSE 100. The programs of both the versions have been written in FORTRAN. It could be run on any computer ANSI standard FORTRAN90 compiler. Also the system should contain sufficient memory to accommodate it.

3.2.2 Materials

The following chemicals and salts were used for this research

Viscoelastic Surfactant

Surfactants are usually organic compounds that are amphiphilic and contain both hydrophobic heads and hydrophilic tails. Viscoelastic surfactants are the special class of surfactant that self assembles to form wormlike micelles. Usually the surfactant containing lengthy hydrophobic tail and short hydrophilic head can form WLM at favorable conditions. It contributes to EOR by providing both mobility control and IFT reduction. Since EOR in carbonate reservoirs have to be carried out with highly saline sea water, three surfactants claimed as viscoelastic surfactant by the supplier Akzonobel were screened for it viscoelasticity with 57,000 ppm sea water and the best one among them is chosen. Their molecular structures are given in **Table 2**.They are

a. Tallow Alkyl Amine ethoxylate commercially named as ETHOMIN T-15
b. Erucamidopropyl Hydroxypropylsultaine commercially named as ARMOVIS.
c. Tallow trimethyl ammonium chloride commercially named as Arquad T-50

Surfactants

Surfactants are the surface active agent that lowers the interfacial tension of the medium in which it is dissolved. Conventional class of surfactants are used to formulate S/VES system by combining surfactant of different class with the optimum VES. S/VES is expected to provide ultra-low IFT. The molecular structures of 4 different surfactants are given in the **Table2.** The four different classes of conventional surfactants are

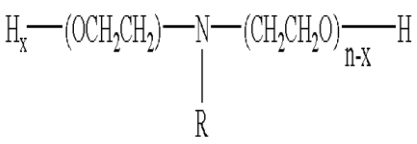
a. Anionic surfactant: The surfactants that can dissociate to yield a surfactant ion whose polar group is negatively charged are classified as anionic surfactants. The anionic surfactant used in this research is glycolic acid ethoxylate lauryl ether
b. Cationic surfactant: The surfactants that can dissociate to yield a surfactant ion whose polar group is positively charged are classified as cationic surfactant. Cationic surfactant used in this research is Alkyl trimethylammonium bromide
c. Nonionic surfactant: The surfactants whose polar group is not electrically charged are classified as nonionic surfactants. Non-ionic surfactant used in this research is cosmacol N II-9 , C12-13- branched and linear ethoxylated
d. Zwitterionic surfactant: The surfactant molecules that contain both positively and negatively charged group are classified as zwitterionic surfactants. Zwitterionic surfactant used in this research is 3-(N, N-dimethyl-myristylammonio) propanesulfonate

Polymer

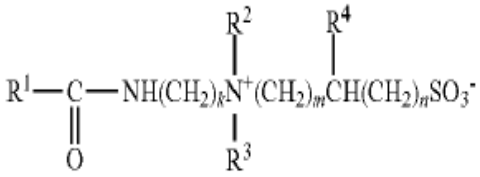
Polymer is a large molecule composed of many monomers. Polymer provides viscosifying power to the medium in which it is dissolved. Polyacrylamide commercially

called as FLOPAAM 2430 S provided by SNF is used. Its structure is shown in **Table 2**

Table 2: Molecular structure of (a) VES-1, (b) VES-2, (c) VES-3, (d) Anionic Surfactant, (e) Cationic surfactant, (f) Non-Ionic surfactant, (g) Zwitterionic surfactant, (h) Polymer



(a)



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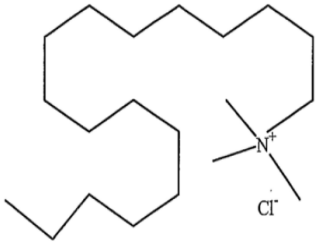

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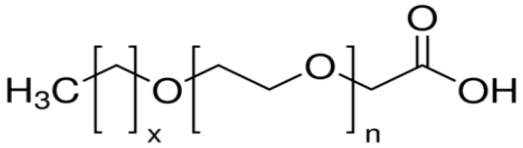

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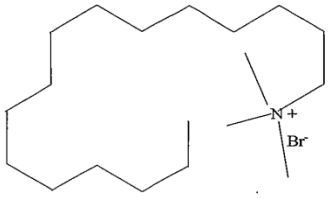

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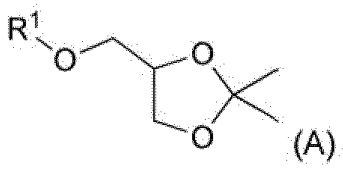
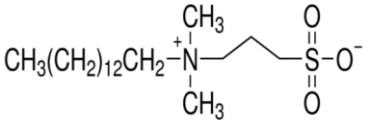


(f)



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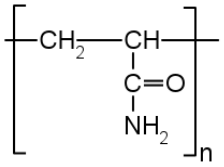


(h)

Salts

Salt is mineral substance. Salts are used for the preparation of sea water and formation water. The salts used in preparing the saline solution in this research are

a. Sodium Chloride ($NaCl$)
b. Magnesium chloride ($MgCl_2$)
c. Sodium bicarbonate ($NaHCO_3$)
d. Calcium chloride ($CaCl_2$)
e. Sodium sulphate ($Na_2S_2O_4$)

They are used to prepare sea water and formation water as per the compositions given in **Table 3 and 4**:

Table 3: Sea water (Sw) composition

Ions	Concentration (ppm)
Na^+	18,300
Ca^{2+}:	650
Mg^{2+}	2082.729
Cl^-	32,200
HCO^{-3}	120
SO^{-4}	4290
Total	57,000

Table 4: Formation water (Fw) composition

Ions	Concentration (ppm)
Na^{+}	59,491
Ca^{2+}	19,040
Mg^{2+}	2439
Cl^{-}	132,050
HCO^{-3}	354
SO^{-4}	350
Total	213,734

Reducing Agent

Reducing agent also called as reductant is the element that donates electron to another species. Since it loses the electron, it oxidizes itself. Oxidizing agent are the one that accepts electrons, since it accepts electron it reduces itself. Traditionally, reduction is defined as the removal of oxygen from the compound. Oxidation is defined as the acceptance of oxygen by the compound. Armovis, identified as the optimum VES contains unsaturated, highly active, hydrophilic tail that is prone to accept oxygen from the medium and undergoes oxidation during hostile aging at high temperature. So, to prevent oxidation and preserve the tail, reducing agent has to be added to remove the oxygen and hence, VES/R system is formulated to optimize the thermal stability. Reducing agent used in optimizing thermal stability of VES is sodium trisulphate.

3.3 VES, S/VES and VES/P Systems

In surfactant polymer flooding, surfactant mobilizes the oil and polymer provides the mobility control. VES as single fluid could provide both. VES is a sensitive fluid whose behavior changes abruptly in accordance to the input. VES is a living polymer which is sensitive to the presence of electrolytes and other surfactants. Surfactant might synergize with VES to induce intense mobilization and polymer might synergize with VES to provide better sweep. Polymer can also provide residual viscosity, in case VES drops its viscosity drastically upon contacting with oil. The methodology adopted in characterizing the viscosity/IFT ratio of VES, S/VES and VES/P systems are detailed in sections 3.7.1, 3.7.2 and 3.7.3 respectively. Sea water is used as the medium in which VES, S/VES and VES/P were dissolved. The composition of it is presented in **Table 3.** The preparation of formation water is also outlined. The preparation of VES, S/VES and VES/P solutions were mostly with sea water and their procedure is outlined.

3.3.1 Preparation of Sea Water

Sea water is used as the preflush, dissolving medium for any chemical in EOR for high saline carbonate reservoir. Hence VES was also prepared with sea water. Most of the tests done in this research were with the solutions made from sea water of 57000 ppm salinity. The preparation of sea water is as follows

1. Pour 1 liter of deionized water in to the beaker
2. Add the salts as per the composition given in the **Table 3**
3. Stir it with the magnetic rod in magnetic stirrer
4. Once the salts get dissolved, the homogeneous solution would be obtained
5. Filter it to get the clear solution

6. Keep the solution static for few hours

3.3.2 Preparation of Formation Water

Formation water was used for saturating the core and to study the effect of salinity on the rheology of VES. In such cases, formation water of 213,734 ppm is used as the dissolving medium. The preparation of formation water is as follows

1. Pour 1 liter of deionized water in to the beaker
2. Add the salts as per the composition given in the **Table 4**
3. Stir it with the magnetic rod in magnetic stirrer
4. Once the salts get dissolved, the thick, denser solution would be obtained
5. Filter it to get the clear solution
6. Keep the solution static for few hours

3.3.3 VES Systems in sea water

Sea water with 57,000 ppm was used as the dissolving medium for surfactants. The reason is that most of carbonate reservoir are highly saline, hence fresh water is not preferred. VES, S and P were added on weight% basis.

To prepare, 0.5% of VES solutions in 120 gm of sea water, follow steps are undertaken

1. Clean the beaker thoroughly with distilled water and dry it.
2. Follow the steps as mentioned previously in 3.3.1 to prepare sea water
3. Add 0.6 gm. of VES into it and pour 119.4 gm of seawater into it.
4. Stir the solution gently using magnetic stirrer until the solutions get homogenized

5. 3- 4 days should be given to VES preparation in order to get the clear viscoelastic solutions.
6. For solutions involving VES, slow speed is preferred to enhance WLM growth
7. VES needs time to dissolve unlike conventional surfactants.
8. Once the clear solution is attained, remove it and keep it static for a day
9. To prepare the VES solution in formation water, just replace sea water as the dissolving medium with formation water. However, formation water doesn't promote WLM growth and the preparation time is shorter.

3.3.4 S/VES Systems in sea water

Surfactant at 0.1 wt. % was added to 0.1% of VES forming 0.2% of S/VES mixture. Four different classes of surfactant namely cationic, anionic, non-ionic and zwitterionic surfactants were added to VES to form four different S/VES systems. To prepare, 0.1%, 0.1% of S/VES systems in 120 gm of sea water, the following steps are undertaken.

1. Clean the beaker thoroughly with distilled water and dry it.
2. Follow the steps as mentioned previously in 3.3.1 to prepare sea water
3. Add 0.12 gm. of VES and 0.12 gm of surfactant in to it the beaker and pour 119.4 gm. of seawater into it.
4. Stir the solution using magnetic stirrer until both the solutions get homogenized
5. For surfactants involving VES, slow speed is preferred so the wormlike micelles get mixed with sea water to attain full viscosity.
6. If the conventional surfactant arrest WLM growth, the mixing doesn't take much time

7. Keep it in stirrer until S/VES systems gets equilibrated
8. Once the clear solution is attained, remove it and keep it static for a day
9. To prepare the S/VES solution in formation water, just replace sea water as the dissolving medium with formation water.

3.3.5 VES/P systems in sea water

Polymer at different wt. % was added to VES forming VES/P systems. To prepare, 0.3% of VES and 0.2% of P systems in 120 gm of sea water, the following procedures are followed

1. Clean the beaker thoroughly with distilled water and dry it.
2. Follow the steps as mentioned previously in 3.3.1 to prepare sea water
3. Add 0.36 gm. of VES and 0.24 gm of polymer in to beaker and pour 119.6 gm. of seawater into it.
4. Stir the solution thoroughly using magnetic stirrer until both the solutions get homogenized
5. For surfactants involving VES, slow speed is preferred so the wormlike micelles get mixed with sea water to attain full viscosity.
6. Polymer can get dissolved at the quick time.
7. VES needs time to dissolve unlike conventional surfactants.
8. However, VES/P systems took 2 days to dissolve.
9. Once the clear solution is attained, remove it and keep it static for a day
10. To prepare the VES/p solution in formation water, just replace sea water as the dissolving medium with formation water.

3.4 VES Screening

EOR fluids need to be compatible in the harsh reservoir conditions. Harsh conditions in the carbonate reservoirs preclude the conventional applicability of chemical EOR methods. High viscosity meant for mobility control and low IFT meant for oil mobilization are the two main parameters that any formulation in chemical EOR is desired for improving the macroscopic sweep and microscopic displacement efficiency. As opposed to behavior of conventional chemical EOR fluids, VES performs better with higher salinity (Degré, Morvan et al. 2011). WLM formed by self-assemblance of VES in salts could provide both mobility control and mobilization enhancement. Certain conventional surfactants become incompatible in the presence of salts. Hence WLM growth indicative of good compatibility and viscoelasticity were ascertained visually along with viscosity and IFT measurements for screening the best VES. VES solutions were prepared with sea water of 57000 ppm. The temperature of 50℃ was used in the study. Three viscoelastic surfactants commercially named as Ethomin, Armovis and Arquad labelled as VES-1, VES-2 and VES-3 are screened for

a. Compatibility.
b. IFT.
c. Viscosity.

IFT tensiometer was used for measuring the IFT reduction and rheometer was used for measuring the shear viscosity at the shear rate of 5/s, corresponding to fluid flow rate in the reservoir. The procedure for preparing the sea water and VES solution are given in sections 3.3.1 and 3.3.3. The procedure for measuring the shear viscosity and IFT are

outlined in sections 3.5 and 3.6. The best VES should be the one that is compatible with sea water of 57000 ppm and should provide higher viscosity and lower IFT. The best one is chosen from the three surfactants.

3.5 Rheological Characterization

Rheological characterization was done with the rheometer. The details of the equipment are mentioned in section 3.2.1. The schematic of the rheometer is shown in the **Figure 4**. The procedure involved in carrying out the rheological tests starts with the preparation of sea water as given in section 3.3.1. The preparatory procedure for VES, S/VES and VES/P solution in sea water are stated in sections from 3.3.3 to 3.3.5. There are two major types of test used in characterizing the rheological parameters associated with EOR. It includes shear test and dynamic test. Concentric cylinder was used as the geometry in the rheometer. It include

1. Shear test: This test is carried out by fixing the shear rate that is corresponding to the fluid flow in the reservoir. It measures the viscosity of the shearing sample. The bob rotates at the prescribed shear rate, shearing the sample in the cylinder. The sheared sample's viscosity is measured.

   Several tests can be carried out with this

a. Flow sweep: by fixing the temperature and time, flow rate is varied to measure the potential of EOR fluid's shear thinning capacity
b. Temperature ramp: by fixing the shear rate and time, temperature is varied to measure the stability of EOR fluid
c. Time sweep: by fixing the shear rate and temperature, the test is to be ran for specified period to measure the rheopectic property of EOR fluid

2. Dynamic test: This test is carried out by locating the linear viscoelastic region for the sample. Upon locating the linear viscoelastic region and fixing the strain percent, the oscillation test is carried out by varying the oscillation frequency. It measures G'and G" of the oscillated sample. G' quantifies the solidity or elasticity of the sample. G" quantifies the liquidity of the sample. Several tests that can be carried out with this

a. Oscillation frequency test: By fixing the strain% and temperature, angular frequency is varied to measure locate the point of intersection between G'and G".
b. Oscillation temperature ramp: By fixing the strain% and angular frequency, temperature is varied to determine the G'and G"

Procedure for rheological test:

1. Prepare the sea water by following the procedure mentioned in section 3.3.1
2. Prepare the VES solutions, S/VES solutions and VES/P solutions as mentioned in sections 3.3.3, 3.3.4 and 3.3.5
3. Clean the cylinder and bob thoroughly with deionized water
4. Place the cylinder into the geometry and align it correctly by connecting the wires into appropriate socket of the rheometer.
5. Connect the bob to the top portion
6. Choose the concentric cylinder as the geometry
7. Do the zero gap
8. Then lift the bob and pour 23 ml of clear viscous VES solution into the cylinder.

9. Use syringe to pour it
10. Now, click the working gap option to initiate the process.
11. Set the test and parameters as per the need.
12. Close it with the seal, once the test starts to ensure that no evaporation take place.
13. Test can be either shear test or oscillation tests.
    a. Shear tests are more commonly used as it involves the shearing that is corresponding to the fluid flow in the reservoirs.
    b. Oscillation tests are used to characterize the fluid flow in the highly permeable part of the reservoirs such as in fractures.
14. Once the test is finished, save the readings.
15. Lift the bob
16. Click the button in the front panel to initiate the removal process
17. Remove the attached wires from the socket
18. Remove the cylinder and geometry from the system. Clean it.

This procedure applies to all the tests carried out with concentric cylinders. The detailed rheological characterization is done to accomplish the following that are described in sections 3.5.1 to 3.5.5

3.5.1 VES Behavior

VES self-assembles to form wormlike micelles (WLM). Wormlike micelles can expand at favorable conditions generating huge amount of viscosity. The conditions can be controlled or optimized to facilitate the WLM growth that is much needed. The parameters include

1. concentration

2. temperature
3. salinity and
4. Flow rate

By fixing varying one parameter and fixing the others, the sensitivity studies on the shear viscosity of VES was done with the rheometer.

3.5.2 VES vs Polymer as a Mobility Control Agents

Mobility control agents are the EOR fluids that are expected to provide uniform sweep efficiency and to avoid fingering. Mobility control fluid ensures that the injected slugs contact as much as pore volume to facilitate the mobilization of as much oil. Shear viscosity is an important factor that the mobility control fluid should have to do so. However, there are tough candidate reservoirs for chemical EOR, where the low permeability precludes application of certain conventional slugs such as polymer. Hence VES, a living polymer is compared over polymer on the basis of

a. Shear thinning potential
b. Reversible shear thinning
c. temperature

Rheometer with concentric cylinder was used to compare their potential as the mobility control agent. Shear tests were used to compare it.

3.5.3 VES with Polymer

It has been well documented that VES provides the dual function of viscosity generation and IFT reduction (Brand, Hansch et al. 2014). Adding polymer to VES can provide residual and additional viscosity and hence the impact of adding polymer to VES is

studied by measuring its shear viscosity. The temperature, concentration and shear rate were kept fixed.

3.5.4 VES Application for EOR in High Salinity Reservoirs

VES has shown positive influence towards salinity (Degré, Morvan et al. 2011). It increases it viscosity with increasing salinity level. Though the reservoir under EOR process will be preflushed with sea water to remove the formation water, still a lots of formation water remains. So the injected EOR slug should combat it. Carbonate reservoirs contains the formation water of salinity 213,734 ppm. In the previous section (3.5.1), methodology adopted to study the effect of salinity on the viscosity of VES was briefed. The salinity level used corresponds to the distilled water (D.W), sea water (S.W), combined water (C.W) and formation water (F.W). The corresponding salinities are 0 ppm, 57000 ppm, 135367 ppm and 213734 ppm. Combined water was the water made by mixing 50% of sea water and 50% of formation water.

The methodology adopted to investigate the potential of VES in combating the presence of formation water was by varying the preparatory mode of combined water by alternating the mode of mixing of sea water and formation water. The mode of mixing is crucial to replicate the real scenario that could exist while flooding the reservoirs. Two modes of mixing were adopted.

1. In mode 1, F.W was added followed by VES and S.W.
2. In mode 2; S.W was added followed by VES and F.W.

The mode 2 simulates the real scenario, as the injected VES solution should mix with the in-situ formation water. Shear viscosity was measured to determine the effect of increased salinity level.

3.5.5 VES Application in EOR for Fractured Reservoirs

Fractured reservoir provides the easy conduit for the injection fluid to channel through it. Unless the fracture is blocked, the injected EOR fluid cannot sweep and mobilize the oil in the matrix or low permeable portion of the reservoirs. Fluids possessing the viscoelasticity can act as a diverting agent to divert the injected fluid to enter into low permeable region or matrix portion of the dual porosity carbonate reservoirs. Further viscoelasticity of the injected fluid can lead to the displacement efficiency by the dragging mechanism. Viscoelasticity of the fluid can be characterized by running the oscillation frequency tests. Oscillation frequency test should be conducted after locating the linear viscoelastic region through oscillation amplitude tests. The substance possessing viscoelasticity should exhibit the following two phenomenons (Dahanayake, Yang et al. 2004) during the oscillation frequency test in order to be considered as viscoelastic

1. G' should be higher than G" at some points below 10 $\frac{rad}{s}$
2. G' should be at-least higher than 10^{-2} Pascal.

Other properties of VES such as shear thinning and internal breakage with oil are also considered as crucial. Even poor thermal stability may be beneficial. After ensuring the viscoelastic potential of optimum VES, the following methodology is adopted to study

the potential of VES as an EOR fluid for naturally fractured reservoirs. It comprises of three steps

Step 1: To block the fractures, inject high concentration of VES. The injected VES should possess very higher elasticity or solidity to divert the next slugs from entering the fractures. Oscillation temperature ramp tests were carried out to determine the G'and G" from 30℃ to 70℃. Dynamic studies were done without any shearing on the tested sample. Absence of shearing means the fluid in the reservoir is not experiencing any stress. This is possible only if the fluid is propagating in the fracture or highly permeable portion of the reservoirs. Since the study is about the fracture, the oscillation frequency test belonging to the dynamic test was carried out to determine G'and G"

Step 2: Having blocked the fractures, inject low concentration of VES that could get inside the low permeable portion of the reservoirs from high permeable fractures. So the fluid should experience stress and it should relieve itself in response to it. Reversible shear thinning property is essential for both getting inside the tight portion and then sweeping and mobilizing the oil. It is characterized by using the shear tests. Flow sweep test was carried out both forwardly and reversely.

Stage 3: The injected low concentration slug after entering the matrix or low permeable region mobilizes the oil from it. Mobilized oil from low permeable region has to find the way to the production well through the fractures. Internal breaking tendency of VES with oil could be exploited. The VES which is blocking the fracture upon breaking should lose its elasticity and it can be determined by carrying out the dynamic test. The difference

between G'and G" should be lower than step 1. Also poor thermal stability of solid VES may be beneficial for the released oil that is traversing through blocked VES.

3.6 IFT Characterization

IFT characterization was done with the spinning drop interfacial tensiometer. The details of the equipment and the working principle of it are mentioned in section 3.2.1. The schematic of spinning drop tensiometer is shown in the **Figure 5**. The procedure involved in carrying out the IFT tests starts with the preparation of sea water and VES solutions as mentioned in section 3.3.1 and 3.3.3. All the tests were carried out for 10,000 seconds to ensure the values obtained are not unstable.

Procedure for IFT test:

1. Prepare the sea water with the procedure mentioned in section 3.3.1
2. Prepare the VES solutions, S/VES solutions and VES/P solutions in sea water as mentioned in section 3.3.3,3.3.4 & 3.3.5
3. Activate the system by switching on the thermo stat, followed by camera on IFT, and then activate the software
4. Fix the temperature through thermo stat.
5. Remove the knot on both side
6. clean the capillary with distilled by injecting on the right side through syringe
7. Keep a beaker on the left side to collect the effluents
8. Now, fill the capillary with the prepared solution by injecting from the heavy phase inlet

9. Then calibration should be done to know the actual drop diameter from the pixel height of the drop image
10. After calibrating the pixel, save it and fix it for recording IFT.
11. Click the sequential mode of operation for 3 hours at least.
12. Click the auto edge detection
13. Then insert a drop of oil using lengthy syringe
14. Rotate it until the clear cylindrical shape of oil is captured and note the corresponding IFT
15. IFT will be calculated based on equation 5 as mentioned in section 3.2
16. Optimize the rotation speed until the oil turns to the cylindrical shape. Maintain the speed so that oil remain in cylindrical shape
17. Keep measuring the IFT until the cylindrical shape gets stabilized for 3 hours and report the value
18. Save it in the folder
19. Remove the oil by injecting distilled water through the right side of the capillary
20. Remove the knob and clean it with distilled water again
21. Connect the knob on both sides of the capillary
22. If the system is high temperature, set the room temperature and await until it cools down
23. Then close the system by starting reversely with software, computer, IFT tool and thermostat.

Using the above procedure, the detailed IFT characterization was done to accomplish the following that are described in sections from 3.6.1 to 3.6.7

3.6.1 Effect of Concentration on the IFT of VES

IFT reduction between the oil and formation water/injected water is crucial to mobilize the oil. The sensitivity study on the IFT of VES was done by varying the concentration from 0.1% to 1%. Salinity and temperature were fixed at 57,000 ppm and 30℃. This study would help in formulating the viscosity/IFT ratio for various concentrations. The total time period 10,000 seconds is given. Unlike shear viscosity, IFT might not give monotonic results. The procedure for carrying out the IFT experiments is mentioned in section 3.6. The procedure for preparing the sea water is mentioned in 3.3.1 and the procedure for preparing VES solutions is mentioned in 3.3.3.

3.6.2 Effect of Temperature on the IFT of VES

The sensitivity study on the IFT of VES was intended to be done at three different temperatures. The temperatures used were 30℃, 50℃ and 70℃. Concentration and salinity was fixed at 0.5 wt. % and 57,000 ppm. The total time period of 10,000 seconds was allotted. This study coupled with the previous sections 3.6.1, 3.5.1 and 3.5.2 would help in formulating the methodology for determining the viscosity/IFT ratio for different temperature and concentrations of VES systems which is discussed in detail in section 3.7. The procedure is similar for carrying out the IFT experiments as mentioned in section 3.6. The only difference is that IFT measurements need to be repeated by changing the temperature. Once the test is done, cool the system.

3.6.3 Effect of adding Surfactant to VES on IFT

The effect on the IFT of VES was studied by adding a conventional surfactant. The system was studied at 50℃ and at the salinity of 57,000 ppm. The total time of 10,000

seconds was allotted. 0.1% of conventional surfactant was added to 0.1% of VES. The procedure for preparing the sea water and S/VES solution are given in section 3.3.1 and 3.3.4. The procedure for measuring the IFT is stated in section 3.6.

3.6.4 Effect of adding Polymer to VES

The effect on the IFT of VES was studied by adding the polymer. The system was studied at 50℃ with the salinity of 57,000 ppm. The total time of 10,000 seconds was allotted. 0.2% of conventional polymer was added to 0.3% of VES. The sea water preparation and VES/P solutions procedure are mentioned in sections 3.3.1 and 3.3.5. The procedure for carrying out the IFT experiment is reported in section 3.6.

3.6.5 Temperature effect on VES and S/VES system

The effect of temperature on the IFT of VES, S/VES systems was studied at three different temperatures. The temperature includes 30℃, 50℃ and 70℃. The salinity is fixed at 57,000 ppm. The concentration of VES is 0.1%, S/VES is 0.1%, 0.1%. The time period of 10,000 seconds was given. The procedure for preparing the VES and S/VES solution is given in section 3.3.3 and 3.3.5. The procedure for carrying out the IFT experiment is same as reported in section 3.6. IFT measurements have to be repeated by changing the temperature.

3.6.6 Effect of Aging on the IFT of optimum VES

The effect of various parameters on the IFT of VES is studied so far on a small time scale. However, EOR fluids have to sustain the harsh temperature encountered in the reservoir for the longer duration. The effect of aging on the IFT of VES was compared with the IFT of un-aged VES sample. The aging was done at 65℃ for 3 months. The

details of aging are reported in section 3.9.2. The concentration, salinity, temperature and duration of test were fixed at 1%, 57000 ppm, 50℃ and 10000 seconds. The procedure for preparing the VES solution is same as mentioned in section 3.3.3. The procedure for carrying out the IFT experiments is same as mentioned in section 3.6.

3.6.7 Comparison of the IFT of un-aged VES, aged VES and aged VES/R

VES/R system was formulated by adding 0.1% of reducing agent $Na_2S_sO_3$ to 1% VES forming VES/R systems. Reducing prevents the oxidation that is prone to happen during aging. It comes under the thermal optimization and the details are mentioned in section 3.9.3. IFT of the un-aged VES, aged VES and aged VES/R systems were studied. The concentration, salinity, temperature and duration of test were fixed at 1%, 57000 ppm, 50℃ and 10000 seconds. The procedure for carrying out the IFT experiments is mentioned in section 3.6. The procedure for preparing the VES solution is same as mentioned in section 3.3.3 and VES/R solutions is prepared by adding 0.1% of reducing agent into VES solution.

3.7 Oil Recovery Potential of VES, S/VES and VES/P systems

Capillary number is defined as the ratio of macroscopic driving force to microscopic resistive force. Most of the EOR methods are designed to enhance the macroscopic driving viscous force and/or to decrease the microscopic resistive capillary force. So to choose the optimum one among the studied systems, viscosity enhancement and IFT reduction of the systems should be considered. Hence, Viscosity/IFT ratio was chosen as the parameter to characterize fluid's recovery potential. The preparation of VES, S/VES and VES/P solutions are mentioned in sections from 3.3.3 to 3.3.5 and measurement

procedure of shear viscosity and IFT reduction are same as mentioned in sections 3.5 and 3.6.

3.7.1 VES system

In this system, viscosity/IFT ratio of optimum VES was determined. Viscosity/IFT ratio was studied for 5 different concentrations and three different temperatures. The concentration in wt. % includes 0.1, 0.3, 0.5, and 0.75,1. The temperatures are 30℃, 50℃ and 70℃. VES is considered as the single fluid capable of providing dual function. This system ensures there will not be any chromatographic separation associated with the injection of multiple slugs.

3.7.2 S/VES systems

In these systems, four different classes of conventional surfactant were combined with VES forming S/VES systems. Cationic, anionic, nonionic and zwitterionic surfactants at 0.1% were added with 0.1 wt. % of VES to form four different S/VES systems. Viscosity/IFT ratio for these systems was calculated. The temperature was fixed at 50℃. The optimum one among the four S/VES systems is chosen as S/VES opt. Viscosity/IFT ratios of S/VES opt is studied at three different temperatures. The temperatures include 30℃, 50℃ and 70℃. Since surfactant itself is an IFT reduction agent when combined with another IFT reduction agent VES, it is expected that S/VES systems should give ultra-low IFT. It can be perceived that VES in these systems could be similar to polymer in the SP system. The effect of increasing the VES concentration on the IFT and shear viscosity of S/VES system was also studied.

3.7.3 VES/P systems

In these systems, polymer at different concentrations was combined with VES forming VES/P systems. The concentration of VES/P include (0.1%, 0.4), (0.4, 0.1), (0, 0.5), (0.5, 0). The temperature was fixed at 70℃. Since polymer itself is a mobility control agent, combining polymer with another mobility control agent VES should give higher viscosity. It can be perceived that VES in these systems could be similar to surfactant in the SP system.

3.7.4 Comparison of Viscosity/IFT ratio of VES, S/VES and VES/P systems

Having studied Viscosity/IFT ratio of VES, S/VES and VES/P systems, the results are compiled together to find the optimum one at 70℃ and recommended for core flooding. Economics is also considered.

3.8 Viscosity Measurements

Ostwald viscometer was used to determine the shear free viscosity of VES solutions. The detail of the equipment is mentioned in the section 3.2.1. This measurement was used to determine the viscosity of the thermally optimized VES samples subjected to long term aging at 95℃. The methodologies and procedures used in the thermally optimized aging process are described in section 3.9.3.Viscosity measurement is an integral part in thermal characterization and the procedure adopted for the viscosity measurement with the Ostwald viscometer is described below

1. Ostwald viscometers of appropriate size corresponding to the expected viscosity range of the sample should be chosen. The schematic of Ostwald viscometer is shown in **Figure 7.**

2. Clean the viscometer with acetone, distilled water and then dry it.
3. Pour the solution into it up to the specified level
4. Using the sucking rubber, suck the viscous solution until the solution comes upward the upper mark
5. Then note the time while the solution flows between upper and lower mark.
6. Having noted the time, measure the density of the solution. Density of the solution is measured using the small beaker by adopting the mass/volume ratio principle. The pycnometer used for measuring the density is shown in **Figure 8.** The procedure for measuring the density is as follows:
    a. The volume of pycnometer glass is 10ml
    b. The mass of the empty pycnometer is measured with the help of the mass balance
    c. Then pour the solution into the pycnometer and measure the mass of it
    d. The difference between the mass of the pycnometer saturated with the solution and empty pycnometer is calculated as the mass of the solution
    e. Then density of the solution is calculated by dividing the mass of the solution by the volume of the solution
7. Having noted the time and measured the density of the solutions(ρ), the viscosity of the solution is calculated using the simple mathematical equation:

    Viscosity can be calculated using the formulae:

    $\mu = \rho * t * c$……..(6)

    Where

    μ is the viscosity of the solution in cP

ρ is the density of the solution

t is the time taken for the solution to cross the lower mark from upper mark in seconds

c is the constant which is dependent on the type of Ostwald viscometer being used

3.9 Thermal Stability

Thermal stability analysis was done to determine the stability of chemical slugs at the high temperature. Two methodologies are adopted for quantifying it.

1. TGA analysis for short term
2. Aging analysis for long term

3.9.1 TGA Analysis

This analysis gives an indication that whether the sample could with stand high temperature. But it's potential as an EOR fluid can be confirmed only through aging approach which is discussed in section 3.9.2.

The schematic of TGA equipment is shown in the **Figure 9.** The details of the TGA equipment and the working principle of it are mentioned in section 3.2.1. The procedure involved in carrying out the thermal characterization starts with the preparation of sea water as mentioned in section 3.3.1. VES and VES/P solutions preparatory procedure are mentioned in sections 3.3.3 and 3.3.5. The preparation of polymer in sea water is almost the same as VES preparation in sea water. However, polymer takes less time get dissolve in sea water than VES.

Procedure:

1. 30 mg of sample (VES, VES/P and P) is taken Al_2O_3 crucible.
2. It is placed in the holder
3. Nitrogen was purged at the rate of 20 $\frac{cm^3}{min}$
4. Heat the sample from 20℃ to 140℃ at the ramp rate of 5 $\frac{℃}{min}$
5. Measure the degradation in terms of weight loss percent while heating the sample from 20℃ to 140℃
6. VES, VES/P and P systems were tested.

3.9.2 Aging

Until now, the procedure involved in studying the effect of concentration, temperature, salinity and shear rate on the rheological and interfacial property of wormlike micelles has been discussed. All the tests were conducted with in the short time scale. However, EOR is the process where the fluids have to reside in the reservoir for a longer period of time. Shear viscosity and IFT reduction are basic requirement of any chemical EOR slugs. We have investigated the potential of VES as a single fluid to provide them on short time scale. The aim of this study is to investigate whether the VES could retain its unique WLM structure at high temperature and could contribute to displacement and sweep efficiency over a longer period of time. IFT measurement and shear viscosity measurements are used periodically to track the behavior over time. The samples were heated in thermal set up at 85℃. Rheometer and IFT tensiometer were used for the periodic measurement of the shear viscosity and IFT reduction. VES and VES/P systems were used and their concentrations were 1% and 0.5%, 0.5. %. The schematic of the

thermal set ups are shown in the **Figures 10 and 11**. The details of the Thermal set up and the working principle of it are mentioned in section 3.2.1. The procedure involved in carrying out the thermal characterization starts with the preparation of sea water, VES and VES/P solutions. The preparatory procedures are stated in sections 3.3.1, 3.3.3 and 3.3.5.

Procedures:

1. VES/P and VES systems are placed in the three way flask that is placed over the heating mantle
2. The temperature of all the heating mantles are fixed at 85℃
3. Thermometer inserted on the right side of three way flask monitors it.
4. Water was supplied continuously through the tap , that would pass over the condenser
5. Condenser prevents any evaporation
6. Using the vacuum pump, create the inert atmosphere replicating the anaerobic environment of the reservoir
7. Take the samples from the left side of the three way flask
8. Use 50 ml big syringe to squeeze the sample out
9. Take it initially after two hours and perform IFT and rheological analysis.
10. The procedure for carrying out the shear viscosity and IFT measurement are mentioned in section 3.5 and 3.6
11. After taking the sample , create the inert atmosphere again
12. Then take the sample again after 2 weeks and perform IFT and rheological analysis

13. Then take the sample again after 2 weeks and perform IFT and rheological analysis
14. Report the results

3.9.3 Improving the Long term Thermal stability by Formulating VES/R system

Results from the long term stability done at 85℃ indicate that WLM of VES is lost resulting in the loss of shear viscosity. Though IFT reduction ability of the VES still remained, its mobility control effect is lost due to the sustained heating at 85℃. The loss of WLM means the loss of viscoelasticity, shear viscosity, reversible shear thinning etc. VES/P systems separate itself indicating the once the WLM dissociate, it cannot hold the polymer. Based on these results, certain conclusions are made and reported in results and discussions. Importantly, the reason for the loss of WLM is traced, reviewed, analyzed, studied and recommended which is the usage of reducing agent. The reason for the loss of WLM in VES at high temperature aging is the oxidation of carbon-carbon double bond in the hydrophobic tail by the dissolved oxygen (Chu, Feng et al. 2011).

3.9.3.1 Optimization for moderate temperature reservoirs

To improve the thermal stability, sodium trisulphate ($Na_2S_sO_3$) was used as the reducing agent to prevent oxidation. 0.1% of $Na_2S_sO_3$ was added into 1% VES forming VES/R systems and aging were done at 65℃ in an oven. VES, VES/R, were the two systems tested for thermal stability at 65℃ with oven. The concentration of two system tested are 1% of VES, 1.1% of VES/R. VES and VES/R systems were subjected to IFT and shear viscosity measurements. IFT and shear viscosity were measured with IFT tensiometer and rheometer as per the procedure mentioned in sections 3.6 and 3.5.

Procedure:

1. Pour 30 ml of each system in to the voil
2. Measure the initial shear viscosity and IFT of VES sample aged for 2 hours at 65℃
3. The procedure for carrying out the IFT and shear viscosity measurements are mentioned in sections 3.6 and 3.5
4. Having measured the initial IFT and viscosity values of VES system, measure the IFT and viscosity of VES, VES/R system after aging for 3 months at 65℃.
5. Quantify the % reduction in viscosity loss and % reduction in IFT reduction capability of VES system in the absence and presence of reducing agent.
6. Discuss the impact of adding reducing agent
7. Report the potential of thermally optimized VES in sustaining its mobility control effect and mobilization effect for moderate temperature reservoirs.

3.9.3.2 Optimization for high temperature reservoirs

To improve the thermal stability, sodium trisulphate ($Na_2S_sO_3$) was used as the reducing agent to prevent oxidation. 0.1% of $Na_2S_sO_3$ was added into 1% VES forming VES/R systems and aging was done at 95℃ in an oven. VES, VES/R were the two systems tested for thermal stability at 95℃ with oven. The schematic of oven is shown in **Figure 12.** The description of oven is mentioned in section 3.2.1. The concentration of two system tested are 1% of VES , 1.1% of VES/R. VES and VES/R systems were subjected to IFT and viscosity measurements. IFT and shear-free viscosity were measured with IFT

tensiometer and viscometer as per the procedure reported in sections 3.6 and 3.8. Procedure:

1. Pour 30 ml of each system in to the voil
2. Measure the initial viscosity of VES samples after 2 hours of aging at 95℃.
3. The procedure for carrying out the viscosity measurements are mentioned in section 3.8
4. Having measured the viscosity of VES system at 95℃, measure the viscosity of VES, VES/R system after 30 days.
5. Quantify the % reduction in viscosity loss of VES system in the absence and presence of reducing agent.
6. Discuss the impact of adding reducing agent
7. Report the potential of thermally optimized VES in sustaining its mobility control effect.

3.10 Core flooding

Core flooding is the process by which the reservoirs conditions are simulated in the lab and a flood test is carried out on the formation core with the core flooding apparatus to determine the efficiency of the formulated slugs in reducing the residual oil saturation. The details of the equipment are mentioned in section 3.2.1. Two types of oil are left behind after water flooding. One is the residual oil that is swept but not displaced and other is unswept, the bypassed oil. Unswept oil would be higher in the low permeable carbonate reservoirs such as the one used in study. Since the chosen formulation is the VES system which has the potential to both sweep and displace the remaining oil, residual oil saturation encompass both the bypassed and swept but un-displaced oil. In

this research, the optimum formulation chosen based on viscosity/IFT ratio was used as the post water flooded slug to determine the efficiency in reducing the residual/ remaining oil saturation in the Indiana lime stone core. The steps involved in carrying out the core flooding experiments are as follows

3.10.1 Preparation of Core

Indiana Limestone core from the carbonate formation was used in the study. The cylindrical core of length 30.45 cm and diameter 3.8 cm was sliced from bulk core. The core was cleaned using toluene at 80^{o}C. Impurities were removed in the core cleaner by evaporating it. Then core was dried at 75^{o}C. Vacuum was applied to remove air from the core.

3.10.2 Pore Volume Measurement

Before saturating the core, the dry weight of it was measured as 754.94 gm. The core was saturated with the formation water of salinity 213,734 ppm. Saturation was done at 2000 psi confining pressure for 24 hours. The wet weight of the core was then measured as 824.13 gm. The difference in weight between wet and dry core was 69.19 gm. Pore volume was calculated as:

$$Pore\ Volume\ (PV) = \frac{Wet\ Weight - Dry\ Weight}{Density\ of\ Formation\ water} \quad \text{....} \ldots\ldots\ldots (7)$$

Formation water density is assumed to be 1; hence the PV accounting for the difference is 69.19. After saturation, the wet weight was measured and the core was immersed in formation water for ions equilibrium.

3.10.3 Core Loading and Confining pressure

Having saturated the core with formation water, it has to be placed inside the core holder. The core flooding system was ensured for the flooding by carrying out necessary precautions and actions. The core was manually loaded into the rubber sleeve by placing spacers inside it. Then the core placed in the rubber sleeve was loaded into the core holder. The confining pressure, replicative of over burden pressure in the reservoir was applied at 1000 psi and the system was checked periodically for any the leaks. Ensuring that there is no leak, all the related pipes were connected. Formation water was injected and flushing was done to remove any air that got trapped in the lines. 500 psi of back pressure is applied.

3.10.4 Permeability Measurement

Permeability is the measurement of ease with which the fluid flows in the reservoir. The permeability of the core was measured by flowing the formation water at different flow rates (q) and measuring the corresponding differential pressure (dP). The slope (m) of q vs d P is found out and substituted in the Darcy law to determine the unknown value permeability in it.

3.10.5 Measurement of Connate Water Saturation

Having measured the PV of 69.19 ml, the oil was injected 0.25 ml/min continuously until no more water comes out. Measure the amount of water that was recovered by oil flooding. All the four solutions i.e. sea water, formation water, oil and VES solutions were placed in four accumulators. The temperature was maintained at 80℃.

3.10.6 Aging

Having saturated the core with oil, the aging was done for 15 days. The temperature of the system was maintained at 80℃ throughout the process.

3.10.7 Water flooding

After 15 days of aging, oil recovery was started by injecting sea water of 57000 ppm at the rate of 1 ml/min. This is the replicative of the secondary recovery technique called water flooding. Confining pressure was maintained at 2000 psi and back pressure applied was 500 psi. Pressure drop was monitored during whole experiment. The recovered oil was collected in 10 ml graduated tube. Almost 2 PV of water was injected to displace the oil and the recovery was noted. Residual/Remaining oil saturation to water flooding was calculated and the corresponding PV's were noted. The reasons for the poorer recovery are discussed.

3.10.8 VES flooding

Once water flooded residual oil saturation is reached, the direction of pipe was changed, so that the VES can be injected as the next slug. VES 0.5% was injected at the rate 0.4 ml/min. It is injected as a single slug to study its potential to both sweep and displace the oil. The recovered oil was collected in the 10 ml graduated tube placed in front of the exit pipe. The injection of VES was continued, until no more oil was produced. The potential of VES to reduce the residual oil saturation is ascertained and the reasons for their behavior are discussed.

3.11 Reservoir Simulations

Reservoir simulation studies were carried out using the commercial software Eclipse to study the problems encountered while applying the conventional EOR methods to the thin viscous heavy oil reservoirs. Steam flooding and polymer flooding are the major thermal EOR and Non-thermal EOR process applied to develop the heavy oil reserves. Three dimensional reservoir model undergoing steam flooding is built using Eclipse 300 and three dimensional reservoir model undergoing polymer flooding is built with Eclipse 100. The 5-spot pattern is adopted for locating the four producers around the solo injector. The grid dimension and reservoirs parameter for steam flooding and polymer flooding model are same and given in the **Table 5.** The thickness and oil viscosity varies while performing sensitivity studies on steam flooding and polymer flooding model. The operational parameter for steam flooding, polymer flooding, hot water and VES/hot water flooding are given in the **Table 6.**

Table 5: Properties of the base case model

Reservoir properties	Values	Thermal properties	Values
Grid dimension	30x30x3	Thermal conductivity	33 btu/ft/day/°F
Grid cell length	50ft,50ft,200ft	Heat capacity of rock	41 btu/ft^3/°F
Thickness	**20 to 200ft**	Reservoir temperature	125°F
Permeability	1500 mD	Overburden/ under burden Thermal conductivity	30 btu/ft/day/°F
Anisotropic ratio	0.1	Over burden / under burden Volumetric heat capacity	38 btu/ft^3/°F
Porosity	0.3	Reservoir pressure	150 psi
Depth	1500 ft	Oil viscosity	**100 to 3000 cP**

Table 6: Operational parameters for EOR processes

Operational parameter	Steam flooding	Hotwater flooding	Polymer flooding	VES/Hotwater flooding
Maximum Injection pressure	850	850	850	850
Minimum BHP	50	50	50	50
Avg. Injection rate/well (STB/d)	1000	1000	1000	1000
Avg. production rate/well (STB/d)	150	150	150	150
Steam quality (%)	70%	0%	0%	0%
Injection temperature(°F)	450	210	80	210

The sensitivity studies were done on both the models to lineate the effect of thickness on steam flooding and the effect of oil viscosity on polymer flooding. The worst case of thin reservoirs of thickness 20 ft., and higher oil viscosity 3000 cP was considered for the comparative studies between VES/Hot water flooding, steam flooding, polymer flooding and hot water flooding. The project duration is 20 years. VES flooding was simulated from polymer flooding by incorporating surfactants effects into it.

VES are thermally stable (Berger and Berger 2008; Brand, Hansch et al. 2014). VES/hot water flooding was simulated by incorporating the effect of polymers and surfactant together, that are resistant to high temperature. In this case, 2 years of steam flooding has been carried out followed by 18 years of VES/hot water injection together. This work is based on the principle that the injected hot water/VES combination provides dual mobility control. The injected hot water reduces the oil viscosity and injected VES increase the viscosity of the injectant fluid. VES of 1000 ppm was injected along with hot

water for 6 months followed by hot water injection alone for 6 months. It is assumed based on literature (Berger and Berger 2008) that VES remains thermally stable and could retain its viscosity and IFT for 6 months in the presence of hot water. Also it is assumed that hot water reduces the viscosity of crude oil to varying level and hence a separate sensitivity study is made in this regard. The extent to which the heavy oil's viscosity reduction is unknown and hence, the series of cases had been considered by varying the viscosity reduction from 3000 cP to 1500 cP , 1000 cP , 500 cP , 200 cP , 50 cP. The oil recovery due to VES/hot water at each oil viscosity was calculated. Finally, a comparative simulation studies had been carried out between steam flooding, polymer flooding, hot water flooding and VES/hot water flooding on the same reservoir model with the worst scenario of 20 ft thickness and 3000 cP oil viscosity. However for VES/hot water flooding, 2 cases have been considered that hot water reduces the viscosity to 200 cP in one case and just 50% to 1500 cP in another case. All these studies are compared.

CHAPTER 4

VES SCREENING

Chemical EOR fluids should be stable at the higher salinities level encountered in the carbonate reservoirs. Further chemical EOR fluids have to viscosify the injected water to provide mobility control and reduce the IFT between water and oil to mobilize the trapped oil. A single fluid capable of performing this dual function could obviate the need for the injection of multiple slugs that are prone to chromatographic separation in the reservoir. The ideal one should be the viscoelastic surfactant that could generate wormlike micelles (WLM) at that particular salinities level encountered in carbonate reservoirs. WLM can provide both IFT reduction and viscosity. Hence, screening was done based on compatibility, IFT reduction and viscosity generation and the results are discussed in this chapter. Three different surfactants claimed to be viscoelastic as mentioned in section 3.2.2 purchased from Akzonobel were tested for its viscoelasticity with 57,000 ppm sea water. They are Ethomin T-15, Armovis and Arquad T-50 and are named as VES1, VES 2 and VES 3 for convenience in this study. Compatibility was done with both deionized water and saline water to lineate the effect of salts. Gulf sea water has been used in preflushing the Middle East carbonate reservoirs for EOR (Han, AlSofi et al. 2013). During preflushing, high salinity sea water would combat the residential formation water with much higher salinity in carbonate reservoirs and could condition the reservoir. Hence, the brine with the salinity level corresponding to the Gulf sea water was used as medium for preparing the solutions with surfactants that were tested for its sweep

and displacement potential during EOR. Its composition is given in the **Table 3.** The results of screening process based on compatibility, IFT reduction and viscosity generation are discussed in 4.1, 4.2, and 4.3 respectively. The methodology sections 3.3.1, 3.3.3, 3.5, 3.6 details the solution preparatory and test procedure adopted in carrying out these tests.

4.1 Screening based on Compatibility

It is crucial to study the effect of salts on compatibility. VES is sensitive surfactant which might behave perplexingly as opposed to the conventional surfactants. VES works better with salts of increasing concentration (Degré, Morvan et al. 2011). This may work with high saline carbonate reservoirs. Contrarily, if the reservoir is of low saline nature, then the slugs can be injected with fresh water. Hence both deionized water and sea water are used as the medium in preparing the VES solutions and analyzed separately.

From the **Figure 15,** it is clear that VES-1 exhibit a sort of viscoelasticity with deionized water. A bubbly nature is an indicative of it (Dahanayake, Chabert et al. 2011). VES-2 precipitates. VES-3 remains a like a conventional surfactant capable of providing only IFT reduction. Absence of viscoelasticity means, controlled mobility ratio cannot be expected. From the **Figure 16**, it is clear that VES-1 which exhibited viscoelasticity with deionized water precipitates with sea water. Hence salts are detrimental to it. Contrarily but fortunately, VES-2 which precipitated with deionized water exhibit viscoelasticity with sea water which is indicative of its positive WLM growth with sea water. A good WLM growth is also an indicative of the good compatibility between EOR chemical and saline solutions. However, IFT and viscosity has to be measured individually. VES-3 fails to generate viscoelasticity.

Figure 15: VES screening in deionized water

Figure 16: VES screening with 57,000 ppm sea water

4.2 Screening based on IFT Reduction

IFT reduction is an important property by which trapped oil gets mobilized. IFT between the crude oil sample and three different VES solutions were measured using spinning drop Tensiometer. The salinity was fixed at 57,000 ppm. The concentration was 0.3 wt. % and the temperature was set at 50℃. The procedure for preparing the VES solutions and the IFT measurements are mentioned in 3.3.3, 3.3.5& 3.6. The results are shown in the **Table 7.**

Table 7: VES screening based on IFT reduction

VES	VES Number	IFT (mN/m)
Ethomin	VES-1	Precipitation
Armovis	VES-2	0.096
Arquad	VES-3	0.080

From the **Table 7,** it is understood that incompatible VES-1 precipitated while measuring IFT. It could not solubilize the oil and spinning drop tensiometer could not measure it. VES-2 which exhibited with 57,000 ppm sea water gives an IFT of 0.096 mN/m. Although this is not an extremely lower IFT, it is reasonable. Even though, IFT reduction is crucial to improve the microscopic displacement efficiency, viscoelasticity along with reversible shear thinning are deemed to be the additional contributing factors for reducing the residual oil saturation drastically (Brand, Hansch et al. 2014). Lower the residual oil saturation, higher the microscopic displacement efficiency. VES-3 gives slightly the lower IFT of 0.08 mN/m. It has to be noted that VES-3 fails to generate viscoelasticity

which is ascertained in the next section 4.1.3 through rheological studies. To sum up, VES 2 and VES-3 showed positive response in lowering the IFT and VES-1 fails.

4.3 Screening based on Viscosity Generation

Viscosity is important to provide mobility control. It contributes to sweep efficiency. Sweep efficiency is more important than displacement efficiency for heterogeneous reservoirs such as carbonate. Hence viscosity is crucial. The growth of WLM gives viscosity. Viscosity of the three VES was measured with the rheometer at the shear rate of 5/s and are reported in **Table 8.** The procedure for preparing the VES solutions and the shear viscosity measurements are mentioned in 3.3.3, 3.3.5 & 3.5. The salinity, concentration and temperature were fixed at 57000 ppm, 0.3%, and 50℃.

Table 8: VES screening based on viscosity

VES	VES Number	Viscosity (cP)
Ethomin	VES-1	Precipitation
Armovis	VES-2	13.85
Arquad	VES-3	1

Results from **Table 8** indicate that VES-1 that precipitated with sea water could not contribute to both IFT reduction and viscosity. Thus it is discarded. Even though VES-3 provides IFT reduction **(Table 7),** its inability to generate WLM (**Figure 16**) discards its applications as a fluid that could obviate the need for multiple slugs by providing dual function. VES-2 as a single fluid could provide both mobility control and IFT reduction.

Thus it may be the potential replacement to conventional SP slugs that are susceptible to separation problems as will be discussed in section 5.5.5.1.

Based on compatibility, IFT reduction and viscosity build up with 57,000 ppm sea water; VES-2 has been found to be an optimal EOR fluid that could endure and sustain the harsh conditions. Hence VES-2 (Armovis) is screened as the optimum VES and recommended for complete characterization as an EOR fluid.

CHAPTER 5

Characterization of Optimum VES

Having chosen the optimum VES, detailed characterization of VES as an EOR fluid was analyzed. The analysis was done through the rheology, IFT, recovery potential (a form of capillary number) of VES and its variants, thermal stability, static adsorption and core flooding. The associated results are presented in this chapter with the detailed discussion.

The ability of optimum VES to provide mobility control and mobilization at various scenarios were studied through the detailed rheological and IFT characterization. Rheology is the study of flow of fluid and characterizing the rheology of an EOR fluid is vital as the injected EOR fluid has to flow through the well bore region initially and then through the porous media of different heterogeneity. Thus characterizing the viscosity with the rheometer at the typical shear rate corresponding to the fluid flow in reservoirs becomes important. Interfacial Tension is defined as the force acting between the two immiscible fluids that leads to stronger capillarity and restricts the mobility of the oil. Usually after water flooding, the IFT becomes high and would be a decisive factor in releasing the oil. The surface active agents are employed to reduce the IFT between the oil and water. Characterization of IFT is also therefore essential particularly in low permeable carbonate reservoirs. The associated rheological results and IFT results are presented with detailed discussion in the section 5.1 & 5.2 respectively. IFT is a property which comes into play only when the injected EOR fluid contacts or sweeps the residual oil. Rheological characterization is more important that IFT characterization as it involves the characterization of sweep efficiency. Sweep efficiency is more prominent in

the oil recovery of carbonate reservoirs. Further rheology can be used to simulate a variety of conditions in reservoirs and hence it could provide more options for EOR research than IFT characterization could provide. Shear test done with the rheometer can be used to characterize the mobility control potential of an EOR fluid in low permeable reservoirs while dynamic tests can be used to characterize the viscoelasticity and diversion potential of an EOR fluid in extremely high permeable thief zones and fractures. Viscoelasticity can lead to another recovery mechanism in EOR by dragging. Hence using the rheology, several tests were done to accomplish the multiple objectives. Under rheological characterization (section 5.1), following results are presented;

a. Effect of parameters on WLM growth (section 5.1.1)
b. Comparison between VES and polymer as the mobility control agent (section 5.1.2)
c. Effect of adding polymer to VES (section 5.1.3)
d. Ability of VES to expand chemical EOR applicability in highly saline reservoirs (section 5.1.4)
e. Ability of VES to expand chemical EOR applicability in fractured reservoirs (section 5.1.5)

Having characterized the rheology of optimal VES, the IFT characterization was also done and it is vital for the EOR fluid to provide low IFT in the low permeable carbonate reservoirs to reduce the capillarity that strongly traps the oil. The results associated with the measurements of IFT reduction with respect to various parameters are presented throughout in section 5.2.

The results attained while determining the ability of VES, S/VES and VES/P systems to improve the recovery potential in form of viscosity/IFT ratio in EOR at the harsh condition of 57000 ppm and 70℃ is presented in section 5.3. VES is considered as the

a. Single fluid capable of providing both sweep and displacement efficiency.
b. Mobility control fluid in S/VES system by combing VES with surfactants
c. Displacement fluid in VES/P system by combining VES with polymers.

Having identified the optimum combination, its thermal stability was determined on short term through thermo gravimetric analysis (TGA) and long term basis through aging and the associated results are presented in section 5.4.1 and 5.4.2. The studied VES possessing all the excellent property loses it WLM partially at moderate temperature and drastically at high temperature. The reason behind it is studied and rectified. The results associated with the optimization of VES's thermal stability by combining it with reducing agent (VES/R systems) are presented in section 5.4.3. As IFT and viscosity are the parameters that an EOR fluid should retain for long time to enhance the oil recovery, they were measured extensively and reported throughout sections 5.4.2 to 5.4.3. Thermally optimized VES was recommended as an EOR fluid. The details are documented in 5.4.4. Having identified the optimum combination based on viscosity/IFT ratio, its potential to reduce the residual/remaining oil saturation is determined by conducting the core flooding experiments on low permeable core and the associated results are presented in section 5.5. A comparison between the proprietary VES employed by Wintershall and the optimum VES was made. Also a comparison was made between VES and other chemical EOR techniques.

5.1 Rheological Characterization

VES is a living polymer which self-assembles to form Wormlike micelles that is very sensitive to the concentration, temperature, salinity and flow rate (Larson 1999). The results achieved by varying one parameter and fixing the other parameters are presented in section 5.1.1. This sensitivity study is very crucial especially in carbonate reservoirs whose harsh conditions may be the enticing and conducive one for getting the best out of VES. Polymer has been used as the mobility control agent for decades in EOR; however it is highly susceptible to harsh conditions encountered in carbonate reservoirs. Low permeability, high salinity and high temperature encountered in carbonate reservoirs complicate the polymer applications in EOR. Comparative results between the VES and polymer as the mobility control agent are presented in section 5.1.2. The chemistry behind the addition of polymer to VES was studied through rheology and its results are discussed by referencing to the related literatures and are presented in section 5.1.3.

VES is a living polymer whose flexibility can be exploited to defy the conventional belief of limited chemical EOR applicability in harsh carbonate reservoirs. VES can enhance EOR applicability in complex reservoirs. Highly saline and fractured reservoirs are the harsh carbonate reservoirs that limit the applicability of chemical EOR due to precipitation and channeling respectively. The ability of VES to sustain its WLM at higher salinity could expand EOR applicability in carbonate reservoirs that contains high connate water saturation of higher salinity. The results incorporating the measured shear viscosity coupled with visual observation is presented in section 5.1.4. Fractured reservoir is another such candidate reservoir and the results attained with the integrated rheological characterization comprising both the dynamic and shear studies is also

discussed and presented in section 5.1.5. Storage modulus and loss modulus were measured for charactering the potential of VES as a diverting agent. Viscoelastic nature of the VES can be characterized by analyzing the behavior of the storage and loss modulus. In addition to the diversion, viscoelasticity can also lead to improved displacement efficiency which is discussed in section 5.1.5.2. Reversible shear thinning phenomenon is used for characterizing the VES's potential to get inside low permeable region initially and behave dynamically in accordance to the stress encountered in those regions at the reservoir conditions. The methodology sections 3.3.1, 3.3.3 & 3.5 details the procedure and equipment used in carrying out these tests.

5.1.1. WLM Growth

VES is a living polymer which self assembles to wormlike micelles (WLM) which can expand at favorable conditions generating huge amount of much needed viscosity. Wormlike micelles are crucial for obtaining viscosity needed for mobility control. Mobility control is needed for good sweep efficiency. Reservoir undergoing EOR process with EOR fluids have to be swept as much as possible to mobilize the trapped oil to increase the recovery factor. Hence WLM contributing to viscosity is crucial for enhanced performance of the EOR process. However, WLM is sensitive and the growth of WLM can vary depending on the concentration, temperature, salinity and rate (Chellamuthu and Rothstein 2008). So, Shear viscosity was measured by varying the concentration, temperature, salinity and shear rate with the rheometer. The procedures adopted in carrying out this study involves the preparation of VES solutions and shear viscosity measurements as outlined in sections 3.3.1, 3.3.3 and 3.5

5.1.1.1 Effect of Concentration

The effect of concentration on the shear viscosity of optimum VES was studied by varying the concentration from 0.1% to 1%. The temperature ramp test was done with concentric cylinder at five different concentrations separately and their shear viscosities at 70℃ were noted. Five different concentration used in the study were 0.1%, 0.3%, 0.5%, 0.75% and 1%. All the concentrations were in terms of weight%. The salinity, temperature and shear rate were fixed at 57,000 ppm, 70℃ and 5/s. Soak time of 120 seconds and the ramp rate of 5℃/min were allotted. The **Figure 17** depicts the effect of concentration on the shear viscosity of VES. As it seen, viscosity increases with the increase in concentration. VES 1% gives the shear viscosity of almost 74.66 cP whereas VES 0.1%, 0.3%, 0.5% gives the shear viscosity of 3.5 cP, 13.85 cP and 21.26 cP respectively. This could be attributed to the fact, that at high concentration, WLM can grow enormously long and can lead to entanglement. This behavior has been reported in the literatures (Chellamuthu and Rothstein 2008). This makes the solution more viscoelastic. The solutions with higher viscoelasticity would contribute to higher sweep efficiency. But, the optimum concentration has to be chosen based on the oil viscosity that could give effective and controlled mobility ratio. The injected EOR fluid should not finger into the oil and accordingly, the concentration of the fluid should be chosen. EOR is the expensive and full field process. Economics should also be taken into consideration for EOR applications. Since the viscosity of the oil used in the flooding is 12 cP, VES 0.5% giving the viscosity of 21.26 cP at the shear rate of 5/s should be sufficient to sweep the oil.

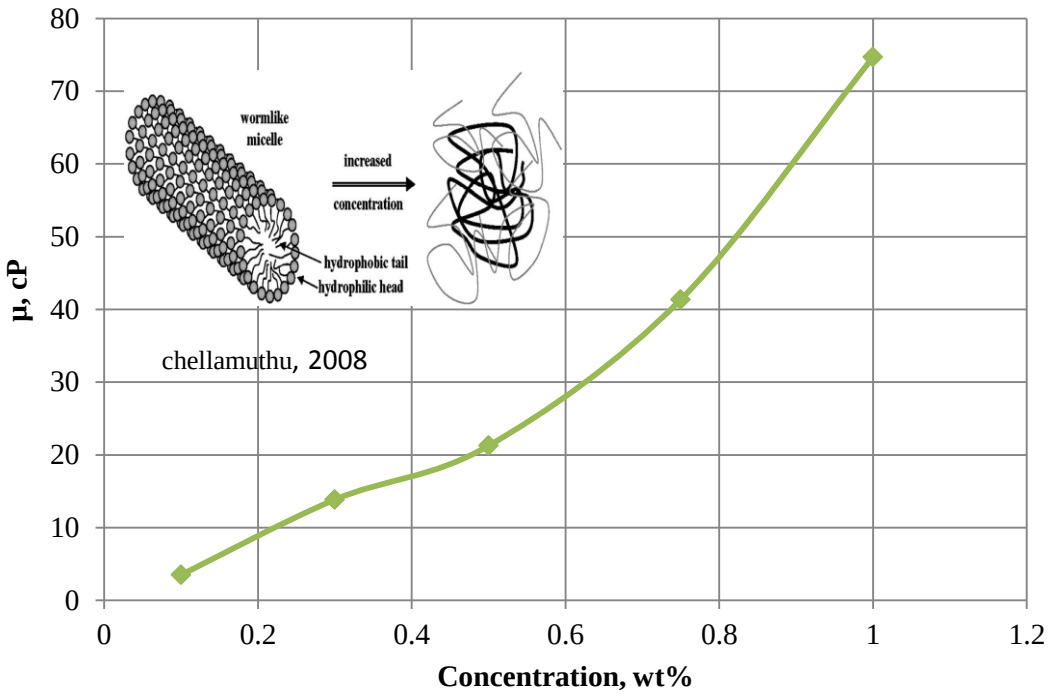


Figure 17: Effect of Concentration on shear viscosity for optimum VES (5/s, 57,000ppm and 70℃)

5.1.1.2 Effect of Temperature

The effect of temperature on the shear viscosity of optimum VES was studied at three different temperatures through temperature ramp test with concentric cylinder. The concentration, salinity and shear rate were fixed at 0.5%, 57,000 ppm, and 5/s. The shear viscosity corresponding to the temperature of 30℃, 50℃ and 70℃ were noted while running the test from 30℃ to 70℃. The soak time of 120 seconds and the ramp rate of 5℃/min were allotted. The **Figure 18** depicts the temperature effect on the shear viscosity of optimum VES. At it can be seen, that the viscosity increases with temperature indicating the thermo viscofying nature of VES. This phenomenon has been reported for the same VES (Armovis) by the supplier Akzonobel while studying it as the stimulation fluid. In fact, viscosification even up to 175℃ is reported. However, long term aging should confirm its long term-thermal stability potential as EOR fluid which is discussed in the section 5.4.2. This viscosifying phenomenon has also been reported for proprietary betaine viscoelastic surfactants developed by Rhodia while shearing at 4/s (Degré, Morvan et al. 2011). The increase in zero viscosity of 500 fold in certain aromatic unilamellar vesicles upon increasing the temperature from 25℃ to 55℃ by heating is reported (Davies, Ketner et al. 2006). The unilamellar vesicles were formed by adding aromatic 5-methyl salicylic acid to cationic cetyl trimethyl ammonium bromide (CTAB). These vesicles changes into long, flexible wormlike micelles upon heating. They attributed the reason that salicylic molecules which are weakly adsorbed should have desorbed upon heating. Desorption should have increased the effective head group area and reduce the tail volume thereby facilitating the formation of WLM solutions. It is

to be noted that the Armovis which itself being a parental VES studied in this research also belongs to the Armotic class.

5.1.1.3 Effect of Salinity

The effect of salinity on the shear viscosity of optimum VES was studied at four different salinities. The four different salinities used were 0 ppm, 57,000 ppm, 135367 ppm and 213,734 ppm corresponding to the deionized water, gulf sea water, combined water and formation water. The temperature ramp test was done to find the shear viscosity of different solutions at 70℃. The concentration, temperature and shear rate were fixed at 0.5%, 70℃, and 5/s. The soak time of 120 seconds and the ramp rate of 5℃/min were allotted. The combined water was formed by mixing 50% of sea water and 50% of formation water.

The **Figure 19** depicts the effects of salinities on the shear viscosity of VES and the **Figure 20** depicts their visual observations. It was observed VES prepared with deionized water doesn't have any shear viscosity **(Figure 19).** In fact it precipitates **(Figure 20)**. The presence of brine is mandatory for the formation of wormlike micelles in viscoelastic surfactant based (cationic, zwitterionic and amphoteric) systems that could entangle to generate shear viscosity (Moss 2006). The reasons are that the surfactants are the amphiphilic molecules composed of long charged hydrophobic tail with an affinity for oil and a short hydrophilic head with an affinity for water. Above the critical micelle concentration (CMC), surfactant molecules spontaneously self-assemble into large aggregates called micelles (Larson 1999). These large aggregates can form variety of shapes depending on the size of surfactant head group, length and number of tails, the salinity of solutions and flow conditions (Israelachvili 2011). Upon decreasing the

effective head group area by preventing the electrostatic repulsions between them, head groups can cluster together resulting in the transformation of spherical micelles to wormlike cylindrical micelles. Salts are needed to screen the electro static repulsion between the head groups (Oelschlaeger, Suwita et al. 2010). Screening of head charges by added salts that could prevent electrostatic repulsion (Chellamuthu and Rothstein 2008). Electrostatic intermolecular attraction is needed for micelles formation. Instead, certain head hydrophobic groups hate water and in the presence of salt-free water, it might have repelled and thus precipitates **(Figure 20)** instead of forming micelles.

Shear viscosity of 21.26 cP is attainable by increasing the salinity to 57,000 ppm **(Figure 19).** VES prepared with gulf sea water facilitates clustered WLM growth and exhibit solid viscoelasticity **(Figure 20).** Thus it is the positive influence towards salinity and has been reported in the previous literatures (Degré, Morvan et al. 2011),(Brand, Hansch et al. 2014). The reason for the improved conforming performance of the viscoelastic surfactant is that, the salts presented in the brine screens the electrostatic repulsion between the head groups and leads to the formation of WLM by clustering it together. Increasing the salt concentration can transform the wormlike micelles from linear to branched and then to interconnected saturated network (Lequeux and Candau 1997).

When wormlike micelles break it pays an energy penalty by forming two new end caps. It increases the electrostatic repulsion to a level strong enough to increase the curvature of an end cap and facilitates the separation of the head groups apart. The phenomenon driving the head group together is the concave curvature of the branch point. The former phenomenon leading to the separation is more intense than the phenomenon driving the head group of the surfactant together without salts (Chellamuthu and Rothstein 2008).

Separation of this head group results in the lowering of viscoelasticity and hence not preferred as a mobility control agent. Thus wormlike micellar solutions may not be preferred for reservoirs with low salinity. In the presence of salts, the head group charges are screened and WLM can form three or four point junctions. This can lead to the sustained branched micelles (Chellamuthu and Rothstein 2008). Branched micelles can provide higher viscoelasticity and are preferred for reservoirs with high salinity. Hence the carbonate reservoirs with high salinity level are the best candidate for employing surfactants exhibiting viscoelasticity.

Further increasing the salinity to 135367 ppm, the shear viscosity drops to around 12.36 cP **(Figure 19).** The visual observation from **Figure 20** also indicates the slight drop in viscoelasticity. Although, the shear viscosity drops from 21.26 cP to 12.36 cP, it is in the acceptable range and would be able to sweep the light oil in the limited area that is not swept by the preflush. It is further discussed in detail in section 5.1.4

Further increasing the salinity to 213,734 ppm, the viscosity drops drastically to around 2 cP **(Figure 19).** WLM is almost lost and VES almost bit watery **(Figure 20)**. The reasons for the drop could be due to the ratio between the salts and VES exceeding the limit. There always exists an optimum range for combining VES and salts. Decrease in viscosity also could be due to the branching of micelles when the electrostatic repulsion is sufficiently screened. If the salts are added further, it may bind with the surfactant so strongly that it may lead to the formation of bilayer. Similar phenomenon has reported for the system formed by adding anionic surfactant to cationic surfactants (Raghavan, Fritz et al. 2002).

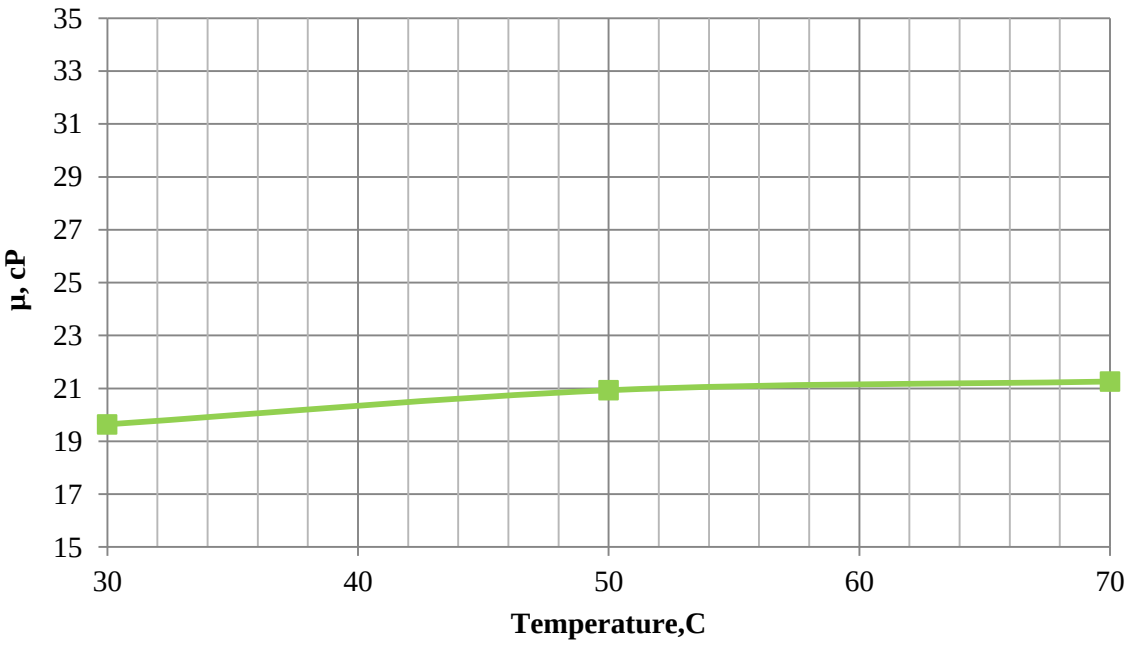


Figure 18: Effect of Temperature on shear viscosity of optimum VES (0.5%, 57,000ppm and 5/s)

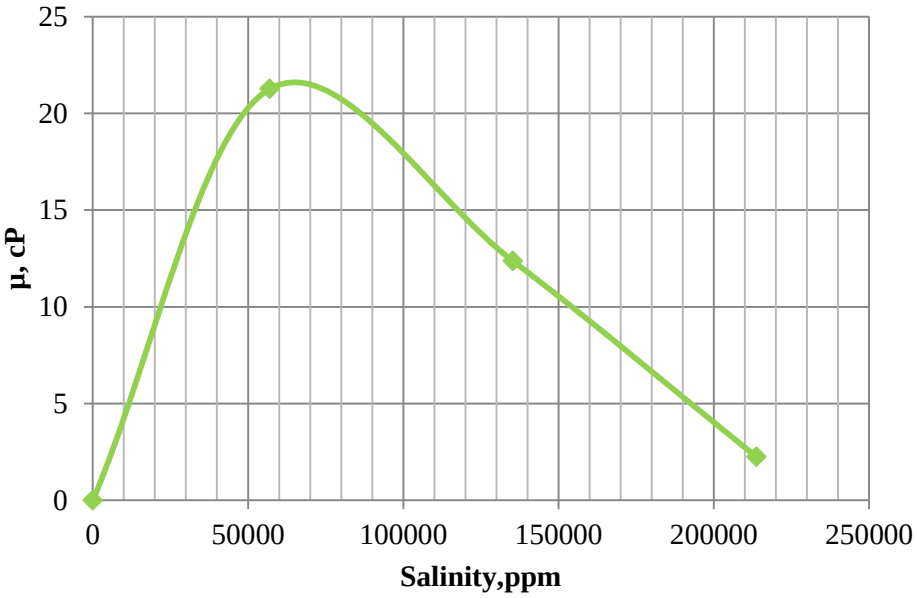


Figure 19: Effect of Salinity on shear viscosity of optimum VES (0.5%, 5/s and 70℃)

Figure 20: Visual observation of VES by varying the salinities

5.1.1.4 Effect of Shear rate

The shear thinning capability of the VES system was studied by varying the shear rate from 0.1/s to 100/s. Temperature and salinity were fixed at 30℃ and 57,000 ppm. Four different concentrations were used. The flow sweep test was done to determine the effect of shear rate on shear viscosity. It is crucial for an EOR fluid to possess shear thinning property. The **Figure 21** depicts the effect of shear rate on the shear viscosity of VES at various concentrations at 30℃. It is clear the wormlike micelles undergo shear thinning. It relieves stress by reptation through Brownian motion as shown in **Figure 22.** The viscosity at lower shear rate is way higher than the viscosity at high shear rate. The viscosities of VES 1%, 0.5%, 0.3% at the low shear rate of 0.1/s are 1174 cP, 302 cP and 69 cP. The viscosities of VES 1%, 0.5%, 0.3% at the high shear rate of 100/s are 10.5 cP, 6.8 cP and 4.64 cP. The slope of VES 1%, VES 0.5% ,VES 0.3% calculated between these two shear rates are -11.64, -2.95, -0.64. This implies that irrespective of concentration, VES can undergo shear thinning. WLM in VES are held together by the weak physical attractions (Chellamuthu and Rothstein 2008). Upon shearing, VES tends to lose solid structure. Therefore it could break easily upon the application of stress. VES 0.1% couldn't viscosify much in sea water and hence could not give the shear viscosity corresponding to the low shear rate of 0.1/s. Injectivity is the measurement of ease with which the formation fluid can get inside the reservoirs (Hyne 2014). The ability of the injected fluid to get inside the reservoir with minimal pressure drop is determined by its potential to undergo shear thinning. Shear thinning is the property by which the fluid thins upon the application of stress. The area around the well bore and the perforated area are the critical places where there is a possibility of poor injectivity for poor shear thinning fluids. The area would be small and would exert the high stress on the fluid

passing by. Unless the fluid undergoes shear thinning, the amount of fluid getting inside the reservoirs for the given pressure drop becomes small and it may affect the overall efficiency of the process such as time delay, delay in front movement, loss of viscous force and loss of reservoir pressure etc. Another potential application of shear thinning fluids is to get inside the low permeable portion of the reservoirs, matrix portion of dual porosity reservoirs etc. which is discussed comparatively with polymer further in section 5.1.2.1

Also, it is clear that using higher concentration of VES would give the higher slope. Though the initial viscosity of the fluid is higher at higher concentration, the easiness that the fluid could get inside the low permeable region would be the same irrespective of concentration. As discussed in the previous section 5.1.1.1, the entanglement is higher at higher concentration. Entangled structures irrespective of the degree entanglement can relieve stress through reptation induced by Brownian motion (Larson 1999).

The **Figure 22** depicts the relieved WLM due to reptation through Brownian motion. Brownian motion is the random motion of various micelles suspended in the WLM structures due to their collision with one another. It keeps moving until relieves itself like the snake movement and hence the name reptation. Hence, WLM might get converted to spherical micelles upon the application of stress. This will facilitate the living nature of VES to penetrate inside the low permeable, tight portion of the reservoir. Low permeable, tight portion of the reservoirs exhibits more stress and the EOR fluids particularly mobility control fluid should lose its rigidness. VES can provide this advantage through Brownian motion.

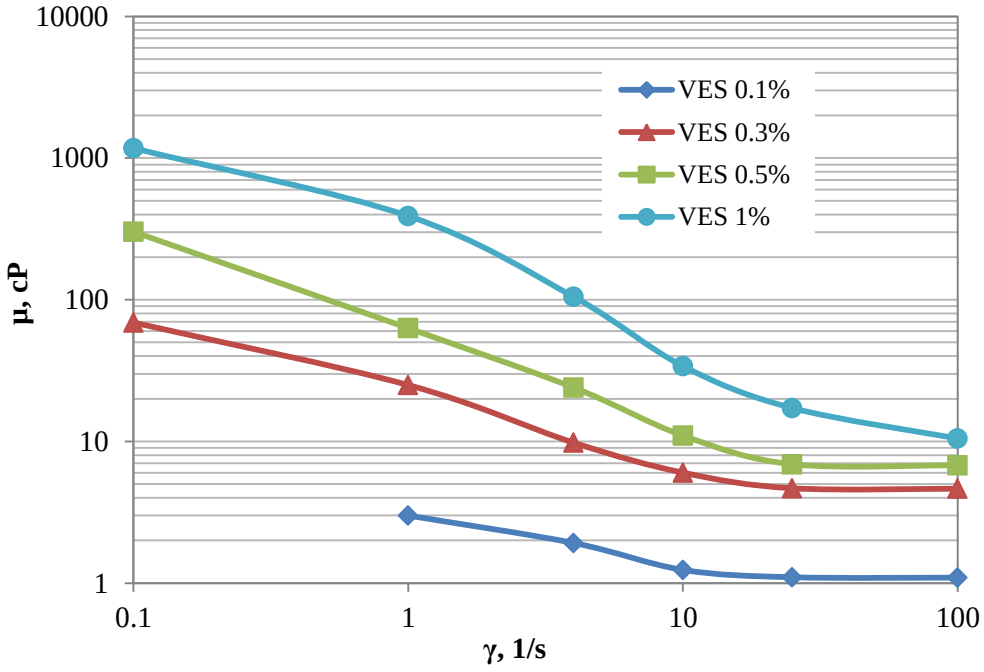
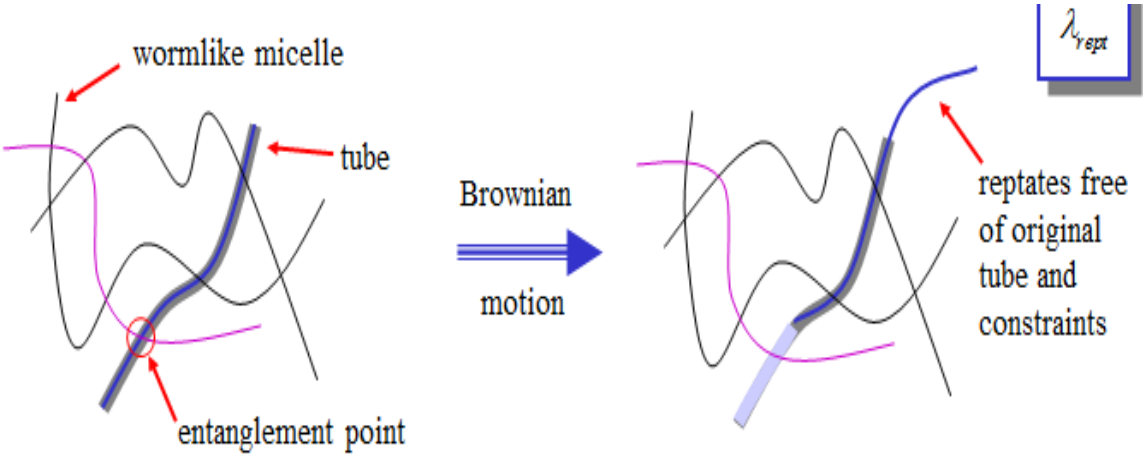


Figure 21: Effect of Shear rate on shear viscosity of optimum VES (57000ppm and 30°C)



(Chellamuthu and Rothstein 2008)

Figure 22: Schematic depicting the reptation of WLM through Brownian motion

5.1.2 Comparison of VES and Polymer as the Mobility Control Agent

Mobility control agents are employed to improve sweep efficiency, prevent channeling and break through. Polymer has been used traditionally as the mobility control agent in chemical EOR for decades. However, polymer flooding has major limitations especially for low permeable carbonate reservoirs. Apart from the injectivity problems around the wellbore associated with polymer flooding, the big molecular size of polymer prevents its entry into the low permeable region of the reservoirs and hence could not sweep those regions. However, carbonate reservoirs are characterized with low permeable zone. So a fluid, capable of undergoing shear thinning upon subjected to stress and reversible shear thinning upon the removal of stress is an ideal option to exploit the tight carbonate reservoirs. Hence the shear thinning and reversible shear thinning potential of VES, the living polymer and conventional polymer is compared through flow sweep tests. The test is carried out with the concentric cylinder by varying the shear rates.

5.1.2.1 Shear thinning potential

Shear thinning capability of VES and polymer was compared. The concentrations of both the fluids were fixed at 0.5%. Temperature and salinity were fixed at 30℃ and 57,000 ppm. Flow sweep test was carried out by varying the shear rate from 1/s to 1000/s. The **Figure 23** compares the shear thinning potential of VES and polymer. The slope of the fluids were calculated by considering the shear rate from 1/s to 100/s. The slope of VES is -0.56 and that of the polymer is -0.39. VES exhibits the higher shear thinning potential than polymer. This property is crucial for the mobility control agent to get inside the low permeable portion of the reservoirs in tight rocks and matrix portion of the naturally fractured reservoirs. Also, this property mitigates the difficulty that the injected fluid

faces, while penetrating the perforated region i.e the injectivity problems. The VES fluid which has the viscosity of around 63 cP at 1/s can beneficially provide the viscosity of 4.9 cP at 100/s. The reasons for the better shear thinning capability of VES over polymer could be attributed to the fact that WLM molecules are clumped together by weak physical attraction. However, polymer molecules are rigid and bonded covalently. So, the WLM molecules could be broken and reformed easily (Chellamuthu and Rothstein 2008). Although, VES excel as the better shear thinning fluid , the difference between the slope of polymer and VES is not that drastic while varying the shear rate up to 100/s. This implies that both VES and polymer can relieve stress especially with Brownian motion at higher shear rate of 100/s. This high shear rate could be experienced only near the well bore. Near well bore regions are more of concern in well stimulation and far well bore regions are more of concern in EOR.

However, shear rate corresponding to the fluid flow in far part of the low permeable reservoirs would be between 15/s to 25/s. Hence the detail comparison between the potential of VES and polymer by shortening the scale of the shear rate from 1/s to 25/s was made. It indicates that the slope – 2.33 is attained for VES whereas polymer provides the slope of just -0.70. This comparison made between VES and polymer by considering the shear range from 1/s to 25/s favors the application of VES strongly over polymer. A little stress will facilitate the entry of VES into it. The reason for the much better performance of VES over polymer in this limited scale is that WLM apart from relieving stress through reptation can also relieve stress in a much lower stress state through breaking and reforming (Rehage and Hoffmann 1991). Branched points in WLM are not fixed at the specific point, be it backbone or any other point. However it is free to slide

along the micelles. However polymer can only relieve stress through Brownian motion which requires higher stress state. The reason behind it is that the branched points formed in polymer are fixed along the polymer backbone that makes the reptation movement difficult and thus requires really high stress state to lower its viscosity. This is the reason that polymer gave the slope of -0.70, while VES gave the slope of -2.33 while varying the shear rate from 1/s to just 25/s. The difference is drastic here and it is implicative that the VES can relieve stress at both high shear rate and lower rate through Brownian motion, breaking and reforming. Because of this, polymer cannot enter the inaccessible pore volume.

Sweep efficiency is more important than displacement efficiency in heterogeneous reservoirs. Sweep efficiency in highly heterogeneous low permeable zone is possible only if the fluid acts in accordance to the applied stress. The higher mobilization of oil experienced during core flooding with VES is reported in literatures (Morvan, Degre et al. 2012),(Brand, Hansch et al. 2014). The reason is in spite of not having ultra-low IFT reduction is its ability to get through low permeable region. However, reversibility of shear viscosity is crucial because the low viscous VES cannot sweep the oil or contact all the pore space, it tends to channel like conventional surfactant. Hence the reversible shear thinning mechanism is crucial which is discussed in the next section 5.1.2.2.

5.1.2.2 Reversible shears thinning potential:

The shear thinning fluid tends to lose its viscosity upon the application of stress. This property is needed near the well bore to facilitate the easy of lot of injectant fluid to get inside with minimal pressure drop. However, the mobility control becomes crucial as the

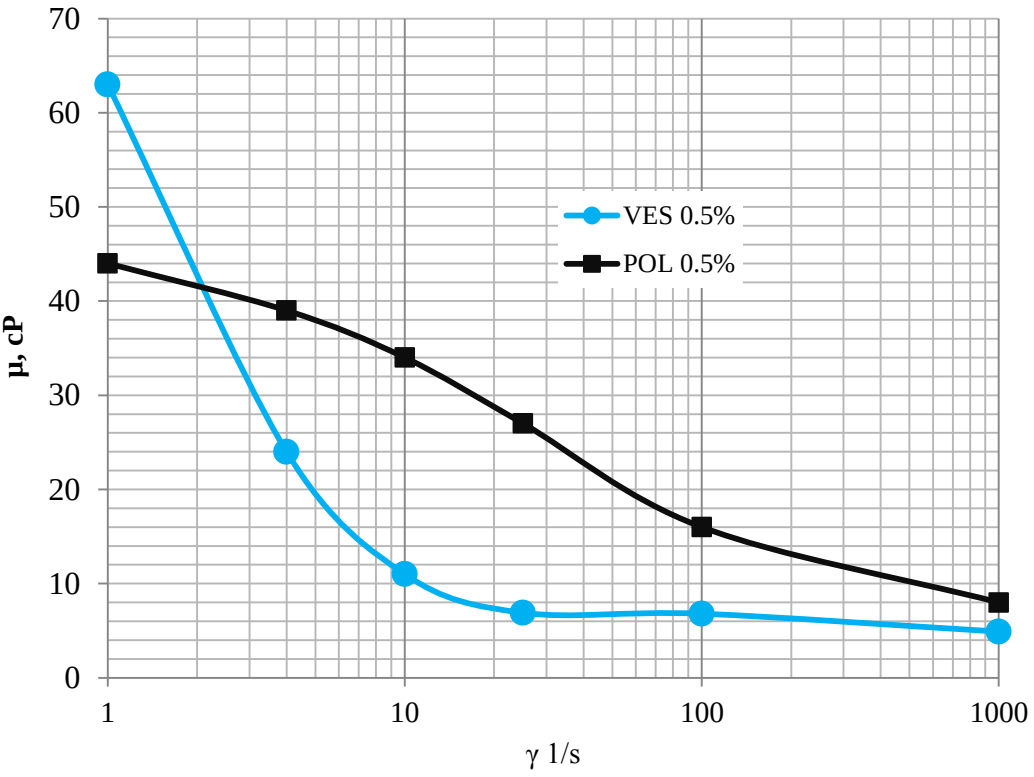


Figure 23: Shear thinning of 0.5% of VES and polymer at 30℃

front moves away from the well bore. Hence the EOR fluids should undergo reversible shear thinning. The potential of VES and polymer to regain its viscosity upon the removal of stress is compared here. It was done by shearing the samples from forwardly from 0.1/s to 100/s and then reversing the shear samples from 100/s to 0.1/s. The test was carried out at 30℃. In the test, equilibration time of 180s and sampling time of 50s were allotted.

The **Figure 24 and 25** shows the reversible shear potential of VES and polymer at 30℃. **Figure 24 and 25** indicates the forward shearing of VES and polymer from 0.1/s to 100/s and the reverse shearing of VES and polymer from 100/s to 0.1/s. Both VES and polymer exhibits reversible shear thinning mechanisms at 30℃. Interesting point to be noted is that viscosity of both the VES and polymer after shearing was higher than the one before shearing. This phenomenon has been reported for viscoelastic polymers (McCormick 1988). However the extent to which the reversed viscosity is different for VES and polymer. It is clear that the restoration of viscosity at the shear rate from 10/s to 1/s corresponding to the fluid flow in the reservoirs (Degre, Morvan et al. 2012) is higher for VES than polymer **(Figure 24 and 25).** The reason is that, both VES and polymer can undergo reptation through Brownian motion. However, polymer molecules do so only at higher stress level are strongly covalent bonded and rigid, while WLM solutions that can do so at even lower stress level are held together by weak physical forces which can break and reform with time (Chellamuthu and Rothstein 2008). The **Figure 26** depicts it. Hence VES is expected to exhibit better reversibility than polymer on a longer scale. Polymer if undergoes severe mechanical degradation for a longer duration on a harsher conditions might not even reverse at all. The reversible mechanism is important in EOR

for enhancing both the injectivity around the well bore and improving the sweep efficiency away from the reservoirs (Sultan, Azad et al. 2014). Higher injectivity is crucial for providing higher viscous force to the displacing EOR fluid.

5.1.2.3 Temperature effect on VES and polymer

The effect of temperature on the VES and polymer was studied comparatively by conducting the temperature ramp tests with concentric cylinder. The behavior of viscosity with temperature was analyzed. This gives us an initial understanding about the long term thermal stability of these systems. The concentration, salinity and shear rate were fixed at 0.5%, 57,000 ppm, and 5/s. The shear viscosity corresponding to the temperature of 30℃, 50℃ and 70℃ of VES and polymer were compared while running the test from 30℃ to 70℃. The soak time of 120 seconds and the ramp rate of 5 $\frac{℃}{min}$ were allotted. The **Figure 27** compares the effect of temperature on shear viscosity of 0.5% VES and polymer. The salinity and shear rate are 57,000 ppm and 5/s. Although the shear viscosity of polymer is higher than VES, it is clear that polymer undergoes thermal degradation and VES exhibits thermoviscosfying nature. The increment in shear viscosity of VES at higher temperature is reported (Degré, Morvan et al. 2011). Polymer poor performance can be attributed to the hydrolysis associated with it in the presence of calcium ions (Levitt and Pope 2008).Although, VES seems to be better than polymer for EOR, long term aging is essential to advocate VES as the mobility control agent in harsh conditions. It is discussed in the forthcoming sections.

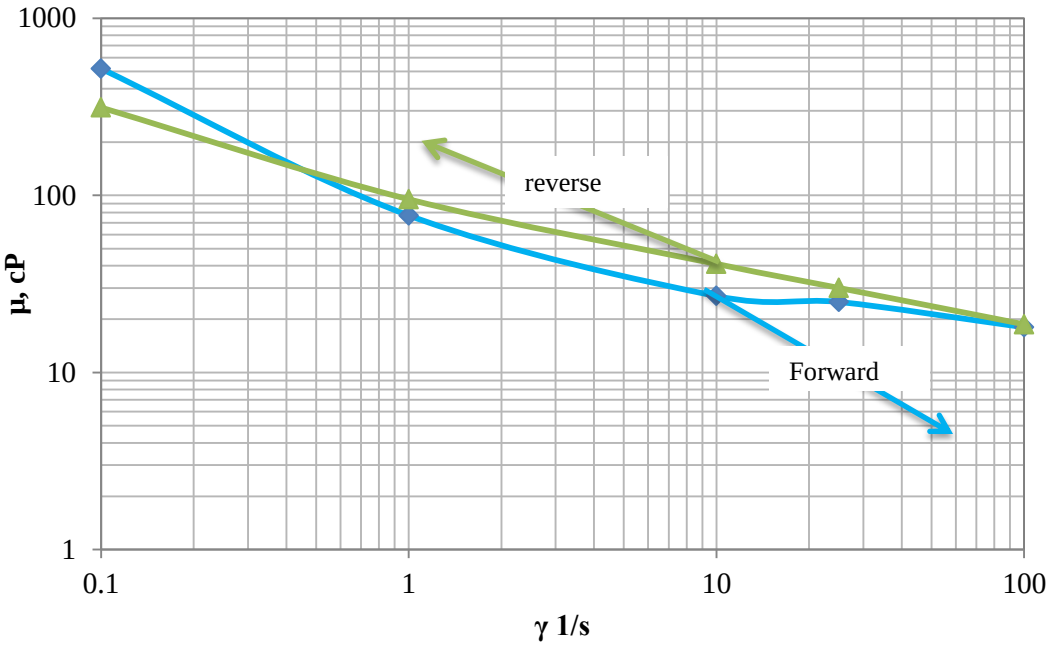


Figure 24: Reversible shear thinning behavior of 0.5% VES at 30℃

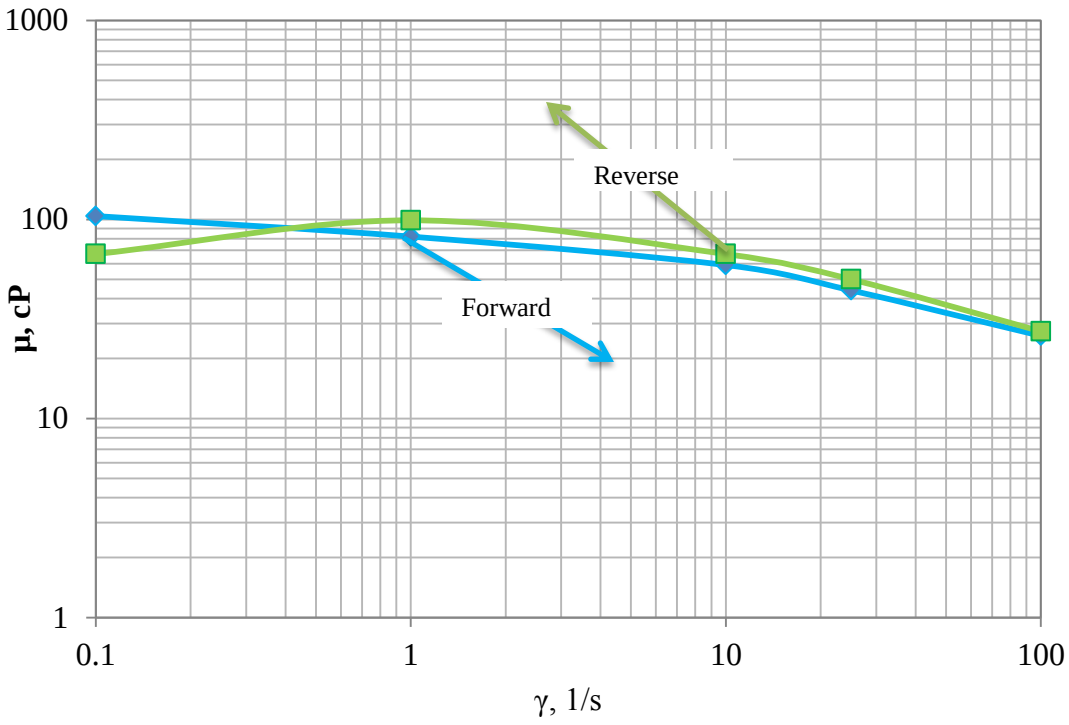
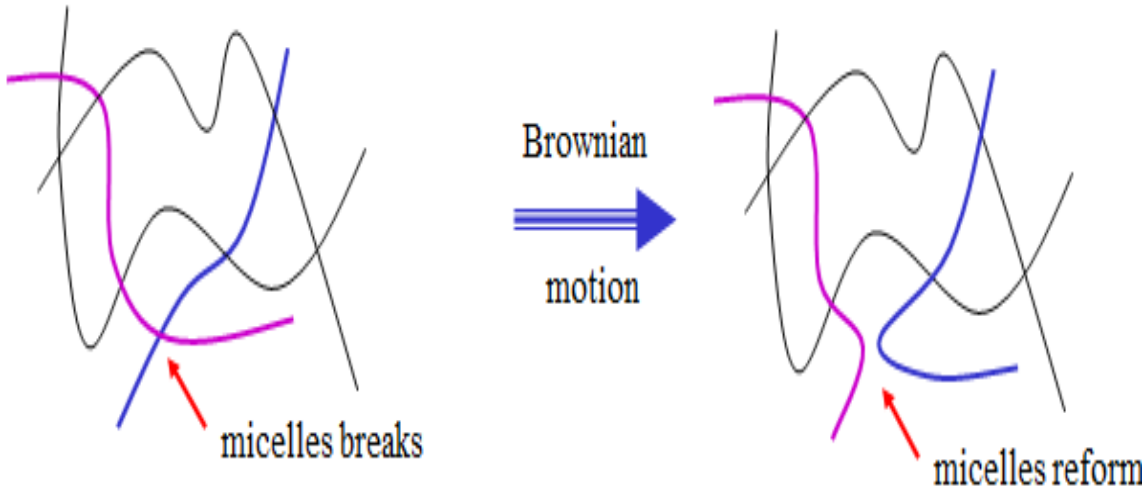


Figure 25: Reversible shear thinning behavior of 0.5% P at 30℃



(Chellamuthu and Rothstein 2008)

Figure 26: WLM breaks and reforms easily due to the weak physical force

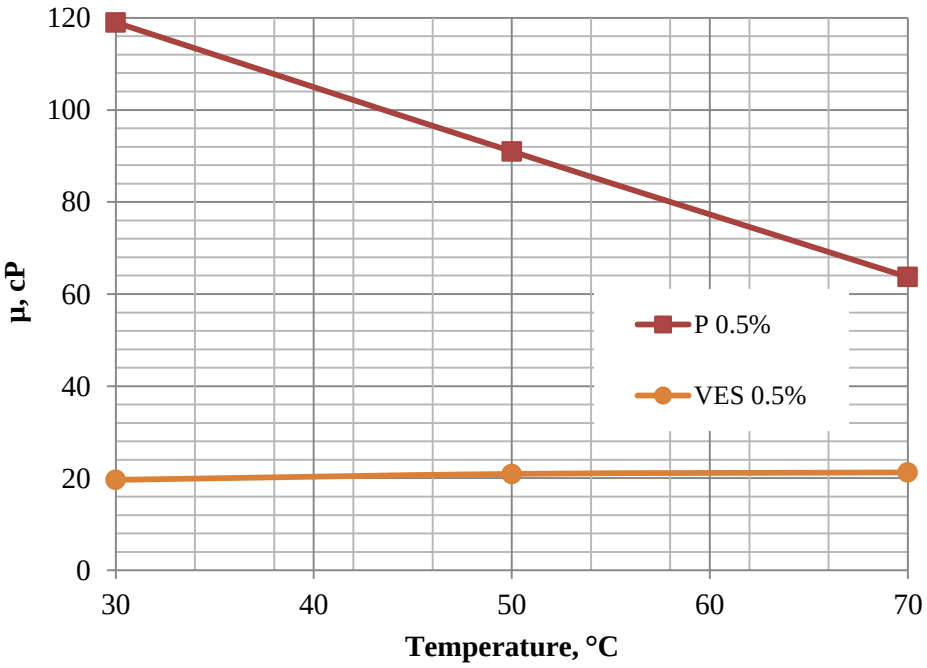


Figure 27: Temperature effect on 0.5% VES and polymer at 5/s and 57000 ppm

5.1.3 Effect of adding Polymer to VES

Polymer is added to VES to formulate VES/P system. Temperature ramp test was carried to determine the shear viscosity of VES and VES/P system at 50℃ and the salinity and shear rate were fixed at 57,000 ppm and 5/s. 0.2 wt. % of polymer is added with 0.3 wt. % of VES and their shear viscosity were measured. The shear viscosity of 0.3 wt. % of VES was also reported at the same conditions. The **Figure 28** depicts the effect of adding polymer to VES at 50℃. VES as a single fluid produce the viscosity of 9.44 cP as indicated by blue marker. VES/P system produces the viscosity of 27.32 cP as indicated by red marker. Hence adding 0.2% of P to 0.3% of VES increases the viscosity of VES by almost 17 cP. Though it is common that higher concentration of viscous fluid gives higher viscosity, the detailed molecular level discussion is essential for VES considering its unpredictable and sensitive nature. Better performance of VES/P over VES could be due to formation of common network as shown in the **Figure 29** that comprises of hydrophobic part of polymer anchored to the elongated surfactant micelles or WLM.

This synergetic effect VES and polymer to enhance viscosity is applicable only with hydrophilic polymers such as FLOPAM that is used in this study. A hydrophilic polymer containing some hydrophobic segments doesn't disturb the cylindrical structure of micelles (Massiera, Ramos et al. 2003). These hydrophilic polymers have penchant to reside in water and contact the micelles part by only hydrophobic units (Shashkina, Philippova et al. 2005). Contacting hydrophobic units intrudes into the micellar portion of surfactant as shown in **Figure 29** and forms the common network to facilitate viscosity enhancement. However, micellar portion has to be wormlike or entangled to hold the contacting hydrophobic part. This is the reason for the higher viscosity of VES/P system

formulated with hydrophilic polymer over VES system **(Figure 28).** The results confirmed the positive synergism which one could expect from adding VES to polymer. VES/P system will really benefit VES as an EOR fluid when the contacting oil contains components that hamper the VES's performance drastically. Polymer can provide residual viscosity which is unfazed by oil. However, its potential as an EOR slug can only be confirmed by long term aging.

Importantly, hydrophobic polymers are not recommended for formulating VES/P systems. Because they contain hydrophobic moieties in each unit that may induce the wrapping of entire polymer chains around the surface of the surfactant aggregates. As the surface/volume ratio of spherical molecules is higher than the rod molecules, the wrapped polymer on the micelle surface induce the formation of spherical structures (Brackman and Engberts 1991). A spherical structure doesn't entangle like rod like micelles and hence could not generate viscosity. Thus hydrophobic polymers should not be considered for the formulation of VES/P systems.

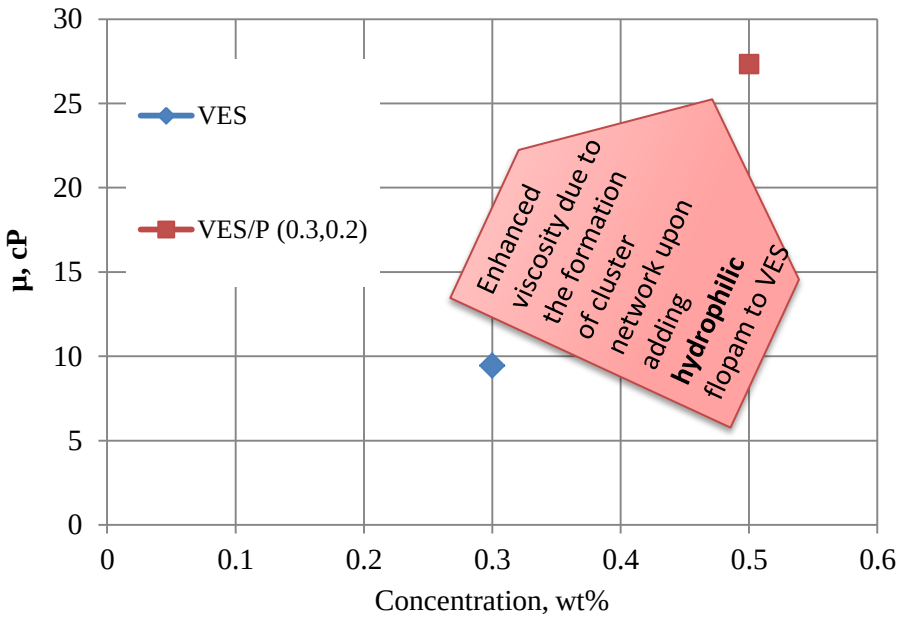


Figure 28: Effect of adding 0.2% of polymer to 0.3% of VES at 5/s

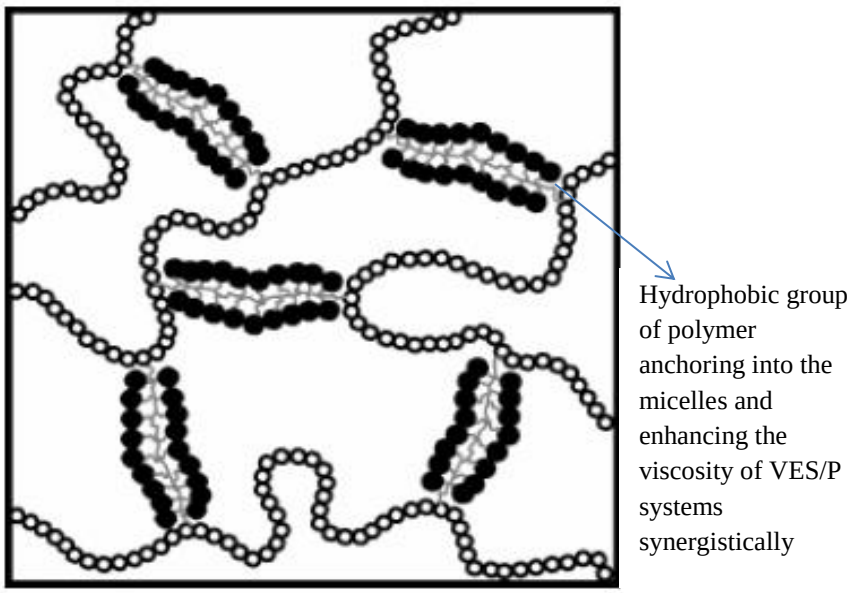


Figure 29: Common network formed by the VES micelles and polymer chains

(Shashkina, Philippova et al. 2005)

5.1.4 WLM solutions for high salinity carbonate reservoirs

Carbonate reservoirs are characterized by high salinity and divalency. Preflushing the highly saline carbonate reservoirs with sea water may not sweep all the formation water. Formation water may be left as the bypassed water due to the channeling of injected preflush. Connate water saturation may also be higher in certain reservoirs. All these could lead to the presence of formation water while flooding the reservoir with chemical slugs.

One of the major limitations of the conventional surfactant and polymer is their susceptibility to the high salinity. Viscosity of the polymer solution drops with increasing salinity level. Most of the conventional surfactant precipitates with increasing salt content. So, carbonate reservoirs characterized by high salinity needs stable chemicals that could sustain the harsh conditions encountered in the reservoirs. Considering the worst case that even after preflushing with 57,000 ppm sea water, the formation water salinity of 213,734 ppm remains in certain portion of the reservoirs, the studies are carried out to determine whether VES could combat it.

Can VES combat the worst case and expand the applicability of chemical EOR in high Saline reservoirs?

To ascertain it, two modes of combined water were prepared. In mode 1, F.W was added followed by VES and Sea Water and in mode 2; S.W was added followed by VES and F.W. The resulting WLM formations are shown in the **Figure 30.** The shear viscosity of VES measured with various salinities is reported in **Table 9**. The shear rate of 5/s and temperature of 70℃ were used. The concentration was fixed at 0.5 wt. %.

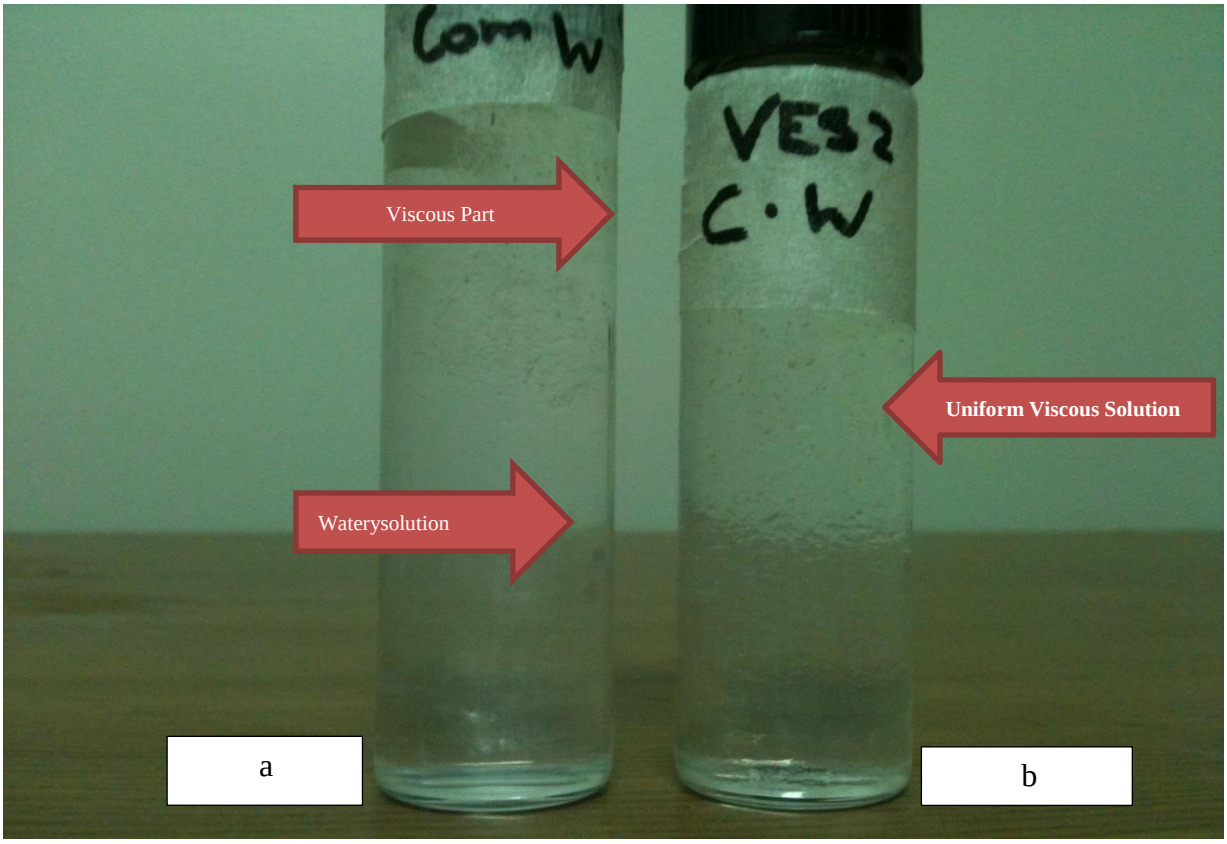


Figure 30: Effect of Mode of preparation of VES: (a) F.W/VES/S.W and (b) S.W/VES/F.W

Table 9: Effect of salinities on VES

Water, Salinity (ppm)	Viscosity (cP)
Deionized Water, 0 ppm	Precipitation
Sea Water, 57,000 ppm	21.26
Combined Water (SW+ FW), 135,367 ppm	12.36 (Possible Scenario)
Formation Water , 213,734 ppm	2.25

From the **Figure 30,** it is clear that the mode of mixing of VES with formation water and sea water has the drastic effect on the viscosity of the solutions. In mode 1, the solution was prepared by injecting VES in formation water and then sea water was added to it. It is clear that this combination is not favorable for mobility control as it results in the separation of VES **(Figure 30, a)** towards the optimum salinity concentration (sea water) in the top. In the mode2, the solution was prepared by injecting VES in sea water and the formation water was added to it. This represents the real scenario in the preflushed reservoir, that the injected viscous sea water solution contacts the remaining formation water later. Higher salinity affects polymer's viscosity (Green 1998). Uniform viscous solution **(Figure 30, b)** and viscosity of 12.36 cP **(Table 9)** attained by this mode of mixing indicates that the added formation water doesn't affect the viscosity of VES prepared with sea water. This property could be exploited to extend the applicability of VES flooding in high saline carbonate reservoirs with high connate water saturations.

5.1.5 Elasticity Characterization and Application for Fractured reservoirs

Rheological tests were carried out to determine the viscoelasticity, reversible shear thinning and internal breakage of oil. Dynamic tests were carried out for measuring viscoelasticity and shear tests for shear thinning potential of VES. Initially for charactering the viscoelasticity, dynamic tests were carried out that involves the determination of linear viscoelastic region through oscillation amplitude test followed by oscillation frequency test and oscillation temperature ramp. Viscoelasticity that can lead to additional recovery through displacement mechanisms in low permeable reservoirs is

discussed in 5.1.5.2 and sweep enhancement and mobilization in fractured reservoirs are discussed in 5.1.5.3 to 5.1.5.5.

5.1.5.1 Determination of linear viscoelastic region:

Linear viscoelastic region was determined by running oscillation amplitude tests. Angular frequency was fixed at $5\frac{rad}{s}$. The temperature was fixed at 30℃. Strain % was kept between from 0.1% and 100%. The concentration of 1% and 2% VES were used. The concentric cylinder was used.

Linear viscoelastic region corresponds to the strain level above which G', the storage modulus begins to deviate from the linear line. It is seen from the **Figure 31**, that up to the strain percent of 15, the G' remains straight for both the concentration. Hence 15% was chosen as the strain% for carrying out oscillation frequency and oscillation temperature ramp tests.

5.1.5.2 Oscillation frequency test:

Having located the linear viscoelastic region, the oscillation frequency sweep test was ran to determine the viscoelasticity of VES. It was done by fixing the strain % of 15, the linear viscoelastic range and by varying the angular frequency from 0.1 to $250\frac{rad}{s}$. It has been reported (Dahanayake, Yang et al. 2004; Dahanayake, Derian et al. 2008) that the viscoelastic substance should have G’ higher than G”, over wide range of points from 0.1 to 10 $\frac{rad}{s}$. Also the value of G’ should be higher than 0.01 Pascal. The **Figure 32** depicts the behavior of G' and G" of VES 1% and 2%. It is clear that both VES 1% and VES 2% exhibit viscoelasticity as per the criteria stated by (Dahanayake, Yang et al. 2004). Up to

10 $\frac{rad}{s}$, G', the storage modulus is higher than G", the loss modulus for both the concentration of VES. Also the value of G' of VES 1% and VES 2% are 0.47 Pascal and 0.19 Pascal which is way higher than the required 0.01 Pascal to be classified as viscoelastic. Hence optimum VES should possess the viscoelasticity and can lead to additional recovery through dragging displacement mechanism which is discussed in this section. Viscoelasticity can also contribute to sweep enhancement in fractured reservoirs which is elaborately discussed in sections 5.1.5.3 to 5.1.5.5

How VES's viscoelasticity can lead to additional displacement recovery?

It has been reported that shear thinning and viscoelasticity are the additional displacement recovery mechanism associated with VES apart from IFT reduction(Brand, Hansch et al. 2014). Viscoelasticity is an additional recovery mechanism that could reduce the residual oil saturation. The residual oil is acted upon by three forces upon viscoelastic fluid flooding (Jiang, Wu et al. 2008).

a. Viscous pressure gradient
b. The retention force
c. Inertia force

Oil blob should create a protruding portion to create enough capillary force to balance the macroscopic driving force as shown in **Figure 33.** The third force inertia becomes imminent when the residual oil blob obstructs the flow of the driving fluid and changes the flow line and the flow velocity in both magnitude and direction. The changes with viscoelastic fluids will be drastic at the protruding portion, induces the micro-inertia force

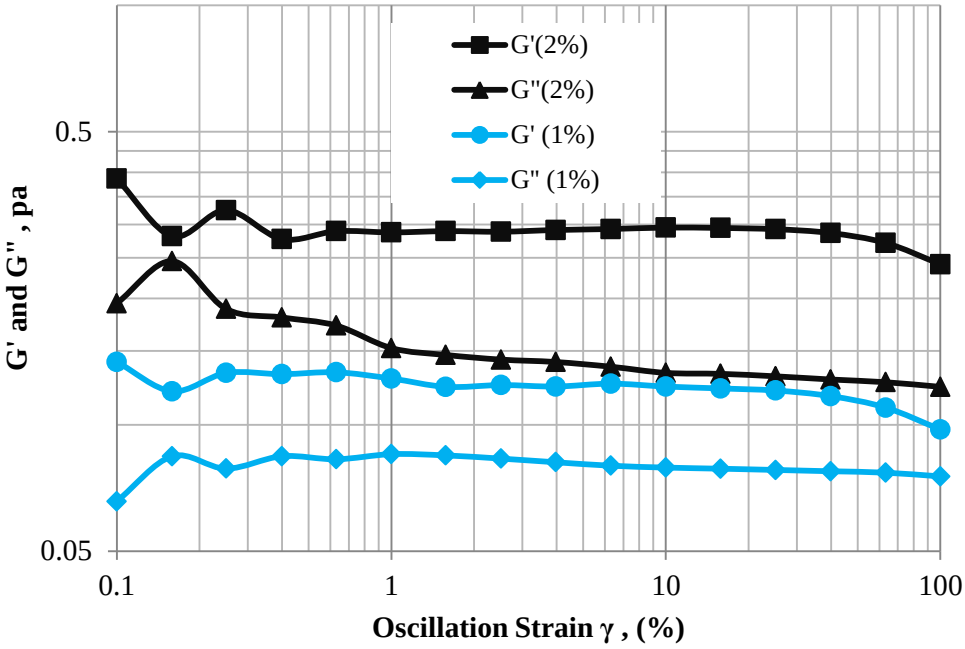


Figure 31: Location of linear viscoelastic region

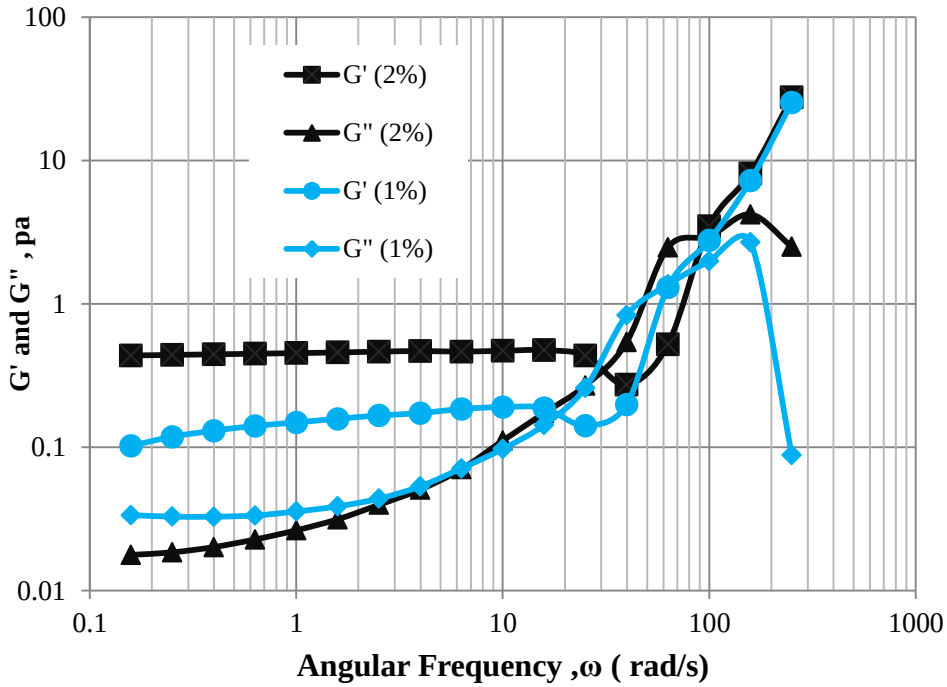
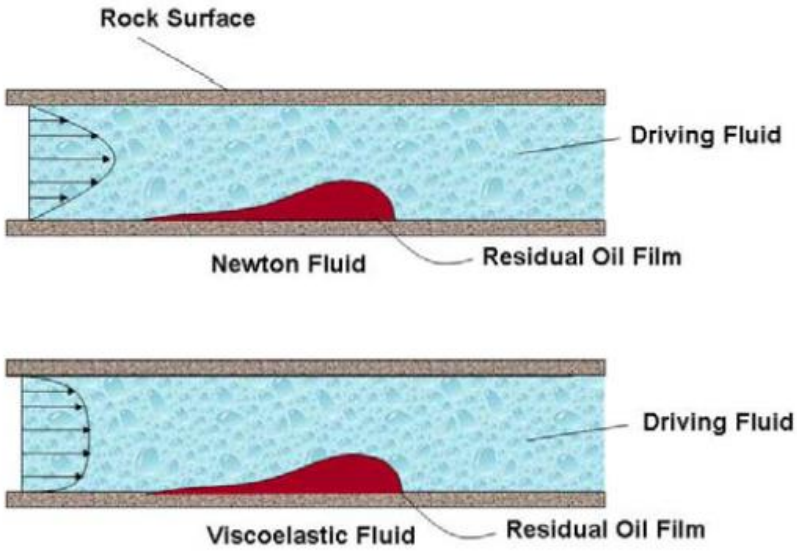


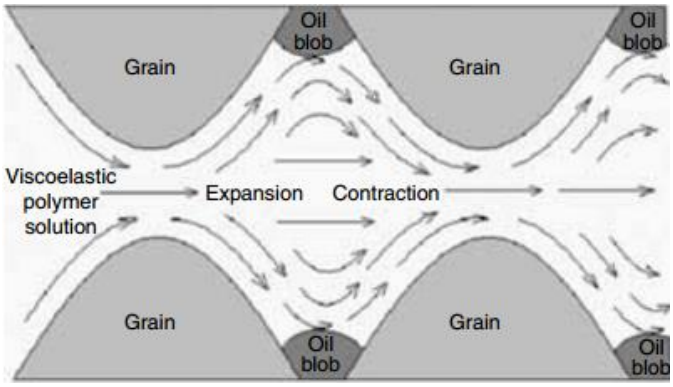
Figure 32: Oscillation Frequency test with 15% strain at 30℃

Newtonian fluids will not get obstructed at the protruding portion and hence there will not be change in velocity as shown in **Figure 33**. The magnitude of the micro-inertia force is proportional to mass and change of flow of velocity. Velocity will be higher for higher elastic fluids. The relaxation time of the high elastic fluid is higher and if the residential time in the smaller pore throat doesn't permit to relax, it will strain itself and changes the flow line's velocity and may drag the oil. This is the property which distinguishes the application of VES as the displacement agent in low permeable reservoirs and as the diverting agent in high permeable portion of fractured reservoirs. The schematic of viscoelastic flow in porous media is shown in **Figure 34.** In high permeable reservoirs, VES expands, solidifies and divert the fluids and in low permeable regions, VES constricts, thins, creates inertial force and drags the oil. This has phenomenon has been reported using viscoelastic polymers based on visual core flooding test done by (Jiang, Wu et al. 2008). With VES, dragging the protruding portion of the oil can be eased by the IFT reduction capacity of VES provided the oil components don't break the VES drastically. The elastic resistance is reported to be more prominent in vicinity of pore throats where there exists the high pressure drop(Han, Wang et al. 1995) and the oil can be dragged easily with the help of existing pressure drop. This aid from local pressure drop in oil dragging phenomena can be exploited to mobilize the oil in the tight micro porous region around the fracture-matrix coupling in fractured carbonate reservoirs. It is understood that displacement efficiency can be attained from viscoelastic materials in the region where there is possibility of heterogeneity on a pore scale. Due to digenesis, carbonate reservoirs are highly heterogeneous on a micro pore scale and could be an ideal candidate for future studies using visualized core flooding.



Jiang, 2008

Figure 33: Forces acting on the residual oil film



Urbissinova, 2010

Figure 34: Schematic of viscoelastic flow in porous media

5.1.5.3 Oscillation temperature ramp for fractures blockage

Oscillation temperature ramp was carried out to determine storage modulus G' and loss modulus G" of the 3 wt. %.VES over range of temperature. Storage modulus is indicative of solidity or elasticity and loss modulus is indicative of liquidity. The angular frequency and strain were fixed at 5 $\frac{rad}{s}$ and 15%. At the ramp rate of 5 $\frac{degree}{minute}$, the temperature was varied from 30℃ to 70℃. Soak time of 120 seconds was given.

The **Figure 35** depicts storage modulus and loss modulus of 3% VES at angular frequency of 5 $\frac{rad}{s}$. It is clear, G' representative of storage modulus is way higher than G" over the range of temperature from 30℃ to 70℃. This higher value of G' could be attributed to the entanglement that happens while using high concentration of VES (Chellamuthu and Rothstein 2008). Entanglement leads to higher elasticity. Higher elasticity is required for the blocking and diverting the fluids.

How higher elasticity could help in improving the recovery in naturally fractured reservoirs?

Recovery efficiency in any EOR process is the multiple of both displacement and volumetric sweep efficiency. Volumetric sweep efficiency can be written as the product of areal and vertical sweep efficiency. The injected slugs preferentially travel towards low resistive path or highly conductive zones as shown by red line in the below **Figure 36.**

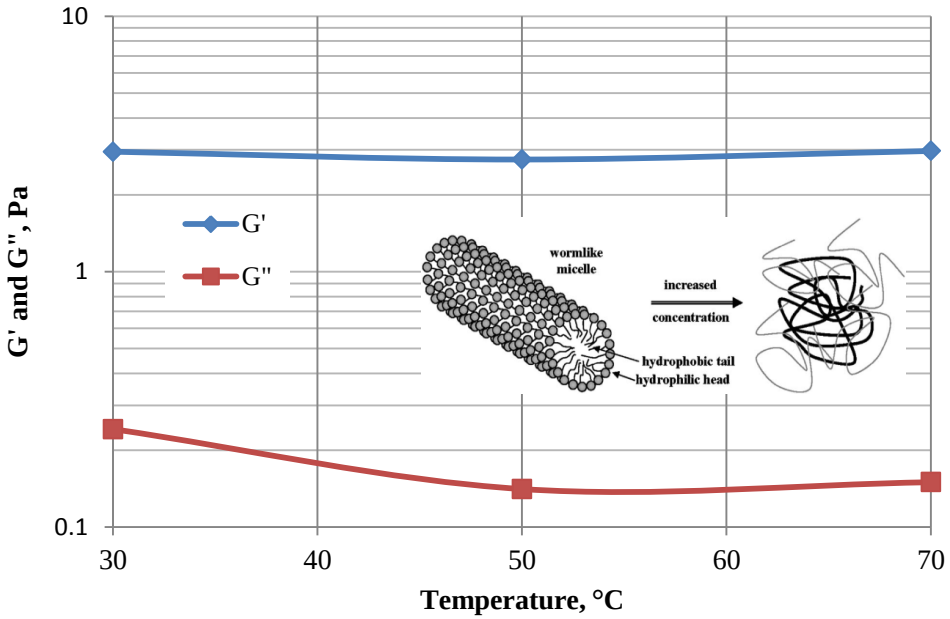


Figure 35: G' and G" for VES 3% at various temperature

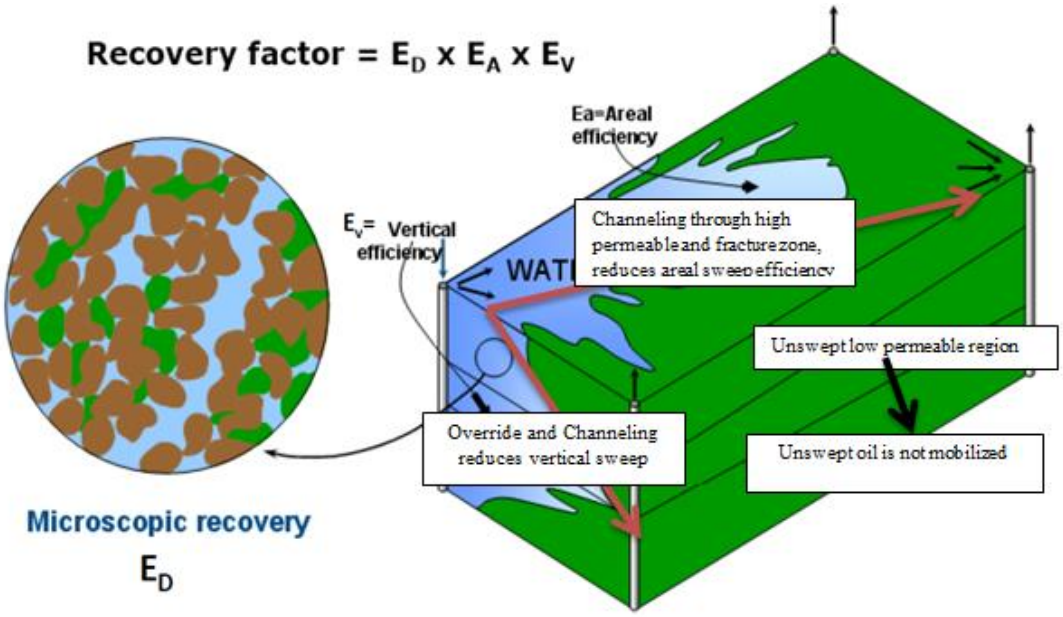


Figure 36: Recovery efficiency during EOR

The presence of natural fractures with high permeability may provide such path (Azad and Sultan 2014). Carbonate reservoirs are characterized by natural fractures (Ehrenberg and Nadeau 2005). Fractures in carbonate reservoirs possess the challenges for chemical EOR (Han, AlSofi et al. 2013). Thus these fractures don't allow the oil in low permeable zone to get swept by the injected slug. Thus it reduces the areal and vertical sweep efficiency. In the heterogeneous reservoirs, sweep efficiency is essential to displace the oil in low permeable zone. Low permeable zone can be perceived as those with green colors where the injected fluid hasn't swept yet. The injected slugs just keep traversing the conducive, high permeable zone for its movement as indicated by bluish region. Thus without contacting the oil in low permeable zone, one cannot expect to mobilize the remaining and residual oil in those zone. So the overall recovery efficiency would be very low. In other words, displacement efficiency is impossible without good sweep efficiency. In heterogeneous reservoirs, contribution from sweep efficiency for EOR is higher than that of contribution from displacement efficiency (Jia, Wanfen et al. 2012). So the high permeable zone needs to be blocked. VES has been used as the diverting agent in well stimulation process (Gomma 2012). The property that favors the applicability of VES as the diverting agent is its uncompromised solid nature that could tightly seal the conductive zone in the reservoir and could divert the slugs approaching it by its resistive strength. As seen from the **Figure 35,** that G' indicated by blue line is higher G" indicated by red line. Hence if high concentration of VES is injected as the initial slug, the following could happen

1. It will go to fracture due to preferential movement
2. could sweep the oil in the fracture due to its dual function of mobility control and IFT reduction **(TABLE 14)**
3. Then could seal the fracture. In high permeable fracture, the VES expands and attains higher viscosity (5.1.5.3)
4. Could divert the further fluids from entering inside (Chang, Qu et al. 2001).

5.1.5.4 Flow sweep test for facilitating the fluid entry into low permeable portion:

The flow sweep test was carried out to determine the reversible shear thinning potential of VES. The test was carried out with low concentration of 0.5 wt. %. The salinity was fixed at 57,000 ppm and the temperature was fixed at 30℃. The flow rate was varied from 0.1/s to 100/s forwardly and the reverse sweep test was carried out on the sheared sample by varying the flow rate from 100/s to 0.1/s. Maximum equilibrating time of 180 seconds and sampling time of 50 seconds were allotted. The result is displayed in **Figure 24.** It depicts the ability of VES to undergo reversible shear thinning mechanisms. VES undergoes forward shear thinning and reverse shear thinning effectively. It relieves stress upon subjected to stress while increasing the shear rate and able to regain almost all its viscosity almost due to its viscoelastic nature upon the removal of stress. The reasons for this behavior were previously discussed in the previous sections 5.1.1.4, 5.2.1.1, and 5.2.1.2. So again, the living nature of VES might help in improving the potential of chemical EOR.

How VES's reversible shear thinning nature can help the EOR in naturally fractured reservoirs?

The initial slug injected with high concentration VES selectively blocks the fracture and high permeable zone. Selective plugging done with will not encourage any further fluid to enter inside and instead will provide the momentum to drive it towards low permeable region that is saturated with oil. Having assured that the high permeable region is blocked through well testing or through other methods, one should switch into the next mode of injection with low concentration VES of 0.5%. EOR is an expensive process and the economics is important. Hence, low concentration of 0.5% should be chosen. VES 0.5% could effectively displace the oil provided it could enter inside the matrix. Its IFT reduction capacity is detailed in the section 5.2.1. Being elastic initially, it cannot get inside the tight entry part of matrix unless it became thinner. Here comes, the undisputed shear thinning potential of VES. The tight or low permeable region exert stress and VES can relieve itself temporarily through various mechanisms as discussed in 5.1.1.4 titled effect of flow rate on WLM growth. The VES can access the matrix or low permeable portion of the reservoirs and can mobilize the oil.

5.1.5.5 Oscillation temperature ramp for studying the internal breaking tendency of VES by released oil:

Oil breaks VES (Berger and Berger 2008). Oscillation temperature ramp mentioned in 5.1.5.3 was again carried out to determine altered storage modulus G' and loss modulus G" of 3 wt. % VES solutions upon adding 5% of oil into VES solution before subjecting it to test. Then the mixture is subjected to the oscillation.

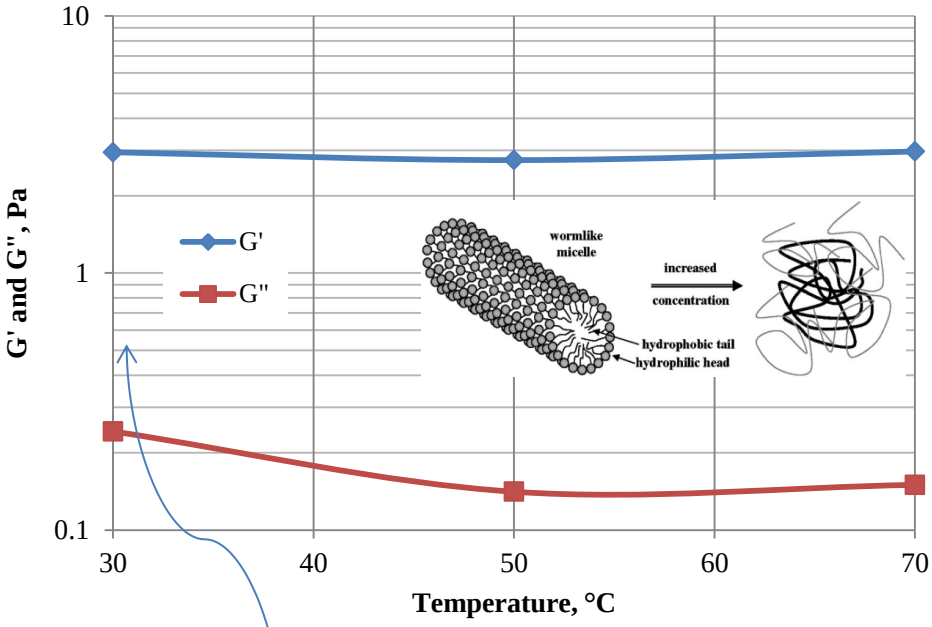


Figure 37: G' and G'' in the absence of oil

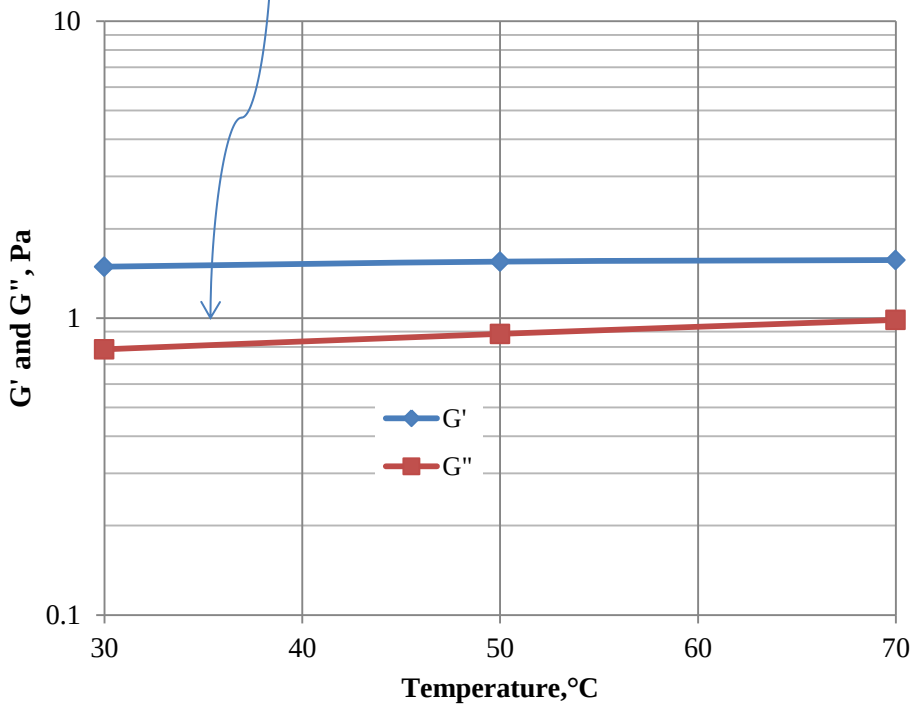


Figure 38: G' and G'' in the presence of oil

The **Figure 37 & 38,** compares the G' and G" in the absence/ presence of oil. As it is clearly seen that G' in the presence of oil has dropped while comparing it with the one which is without oil. Though it still remain viscoelastic as long the G' is higher than G", the released oil could alteast reduce the solidity of plugged VES to a little extent and it can be coupled with the other internal breakers if there is no continuity between the matrix towards the production well.

Another property that can also act as an internal breaker is the poor long term stability of VES at high temperature as discussed in section 5.4.2.1**.** Optimal slug design and detailed reservoir characterization are necessary to exploit these unique properties of VES. It is highly recommended to consider sophisticated characterization techniques.

How internal breaking mechanisms of VES can improve the EOR in Naturally fractured reservoirs?

The oil displaced from the matrix has to find the way towards the production well. Matrix flow will delay the production due to its lower permeability. Hence flowing through the fracture is one option. Though still G' remains higher than G", the G', the solidity decreases and G", the liquidity increases upon the addition of oil **(Figure 37&38).** The release oil can travel through the fracture towards the production well by breaking it. If the reservoir is of high temperature, the poor thermal stability coupled with oil release from matrix can ease the breaking mechanism of the VES blocking the path for oil towards the production well.

5.2 IFT Characterization

In this section, the results attained while characterizing the IFT reduction with respect to various parameters are discussed. The attained results while studying the effect of concentration, temperature, surfactant addition, polymer addition on IFT are presented in sections from 5.2.1 to 5.2.4. The effect of temperature on VES and S/VES is compared in section 5.2.5. The effect of aging on the IFT of VES system is presented in section 5.2.6 and the comparison between the IFT of unaged VES, aged VES and aged VES/R systems were presented in section 5.2.7. Oil of 12 cP was used and 10,000 seconds were allotted. The methodology section 3.3.1, 3.3.3, 3.3.4, 3.3.5 and 3.6 details the procedure and -equipment used in carrying out these tests

5.2.1 Effect of Concentration

The **Figure 39** depicts the effect of concentration on the IFT of optimum VES. The test is carried out at 50℃. The salinity of the solutions was 57,000 ppm. The total test duration of 10000 seconds was allotted. There exists the jump at 0.3%. IFT reduction is a phenomenon where there could be non-linearity (Lakotas, Toth et al., 2007). It is also clear that concentration doesn't influence much after 0.5%. Although, IFT is not ultra-low, VES can contribute to recovery through its viscoelasticity. IFT is very sensitive to concentration, temperature and salinity (Cai, Yang et al. 1996). There exists the non-linearity with IFT reduction through surfactants (Rosen, Wang et al. 2005). It has been reported that packing parameter, salinity and concentration plays the combined role in determining the ranges. For a proprietary amphoteric VES, the non-linearity in IFT with

respect to concentration has been reported (Lakatos, Toth et al. 2007). Micelles in VES are very sensitive that varies with respect to salinity and concentration.

5.2.2 Effect of temperature

The **Figure 40** depicts the contradicting effect of temperature on the IFT of optimum VES. In this study, the concentration and salinity of the solution were fixed at 0.5% and 57,000 ppm. The total test duration of 10000 seconds was allotted. As it clearly seen, the lowest IFT is achievable at 50℃ and then the IFT increases with temperature. IFT is very sensitive to concentration, temperature and salinity (Cai, Yang et al. 1996). The non-linearity of temperature response on the IFT is reported (Lakatos, Toth et al. 2007). The higher IFT at higher temperature could be due to inverse temperature effect on surfactant solubility (Miquilena, Coll et al. 2010), (Karnanda, Benzagouta et al. 2013). Further for VES, the complexity comes in terms of interfacial viscosity (Lakatos, Toth et al. 2007) and short thermoviscosfying nature. Increase in interfacial viscosity leads to increased non-Newtonian behavior or rigid behavior at the interface leading to the unfavorable consequences in the displacement efficiency or IFT reduction (Lakatos, Toth et al. 2007). Further however if WLM is arrested by adding surfactant, then effect of temperature on IFT is opposite which is discussed in section 5.2.5. VES is a sensitive surfactant which can vary its WLM growth in accordance to the various external stimuli.

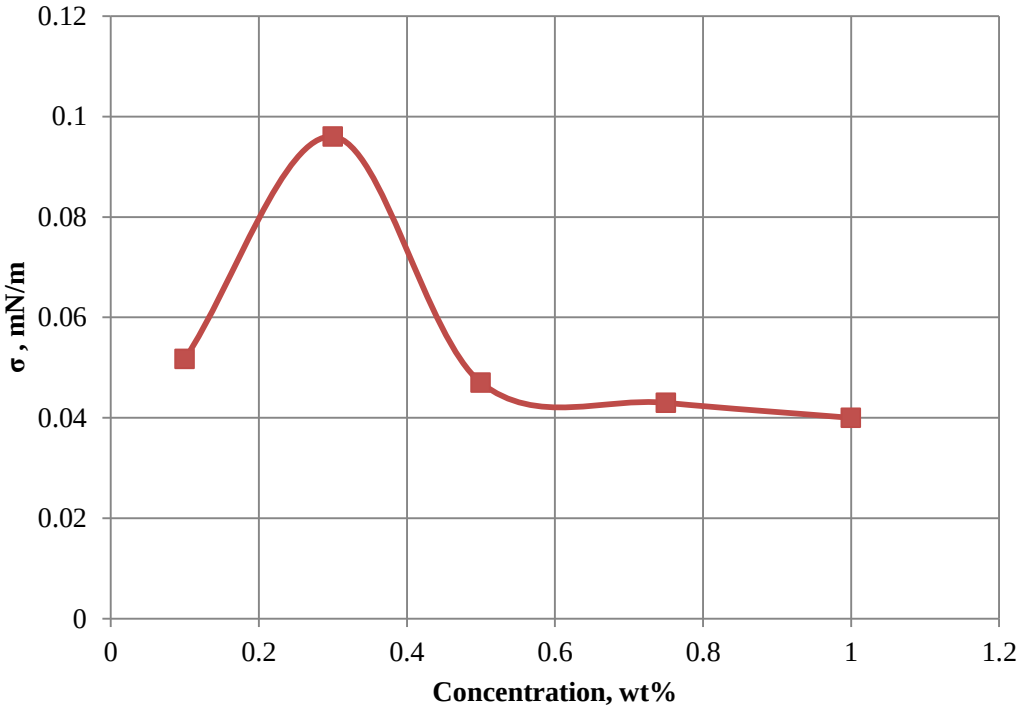


Figure 39: Effect of concentration on the IFT of optimum VES

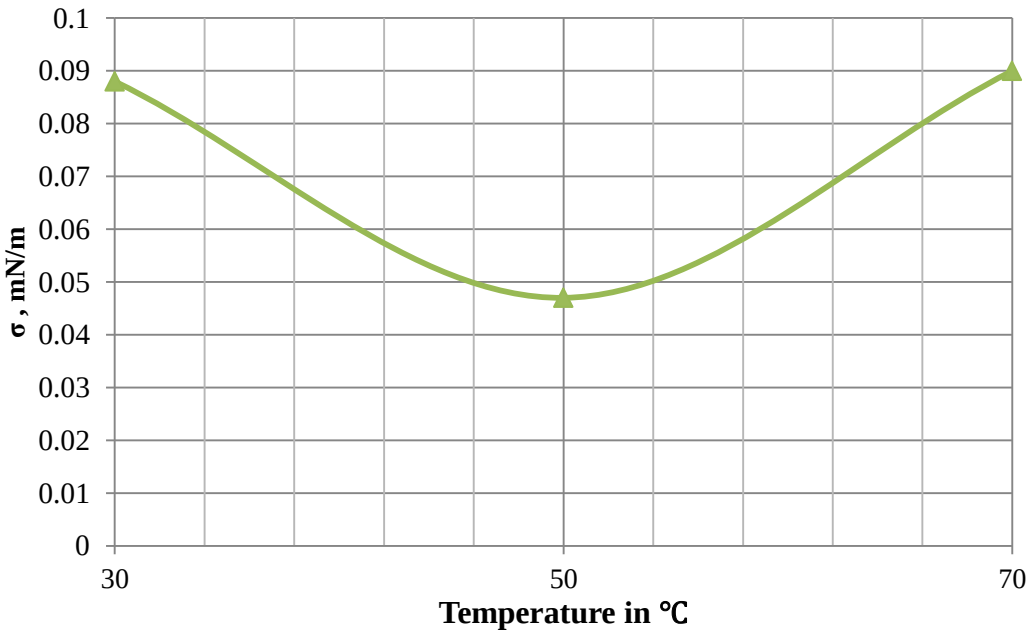


Figure 40: Effect of temperature on the IFT of optimum VES

5.2.3 Effect of adding Surfactant to IFT of optimum VES

The **Figure 41** depicts the impact of adding conventional surfactant at 0.1% to 0.1% of VES on its IFT. The salinity and temperature were fixed at 57,000 ppm and 50℃. As it is clearly seen, the added surfactant negatively impacts the IFT reduction capacity of VES. Similar phenomenon has been reported for the negative synergism while combining VES with the non-ionic surfactant (Lakatos, Toth et al. 2007). It is the packing parameter which is determining the type of micelles formed by the surfactant. Adding an additional surfactant disturbs the micellar packing parameter and might have interacted with hydrophobic portion and jeopardize its efficiency. Also the shear viscosity also got affected for S/VES systems which are discussed in the section 5.3.3.2

5.2.4 Effect of adding Polymer to IFT of optimum VES

The positive impact of adding conventional polymer to VES on macroscopic shear viscosity has been discussed in section 4.3. In this section, the impact of adding polymer to VES on its microscopic IFT reduction is investigated by adding 0.2% of polymer to 0.3% of VES at 50℃ and 57,000 ppm. As it is seen from the **Figure 42,** the impact of adding polymer to VES is not that negative when compared with adding surfactants. However there is a slight increment in IFT which is due to the intrusion of polymer molecules into the micelles as stated by (Shashkina, Philippova et al. 2005) and depicted in the **Figure 29.**

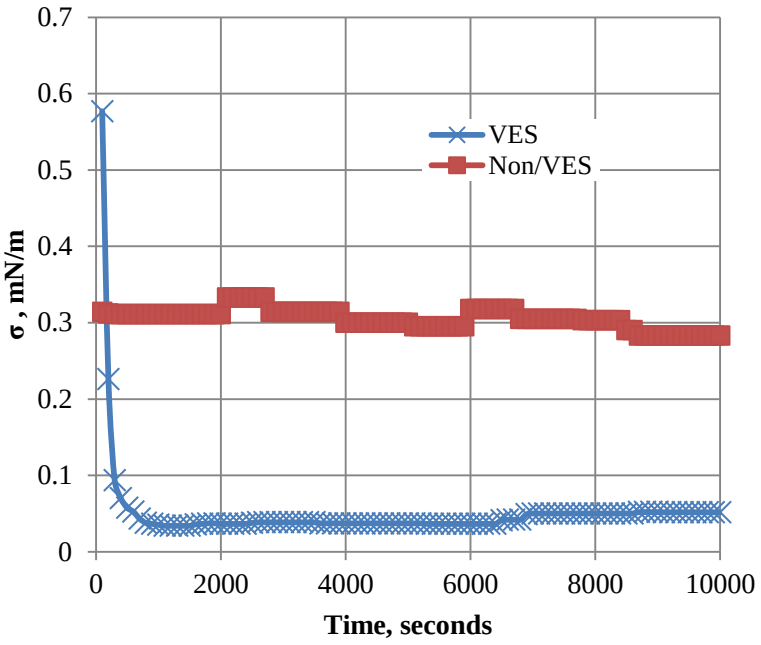


Figure 41: Effect of adding surfactant to VES on its IFT

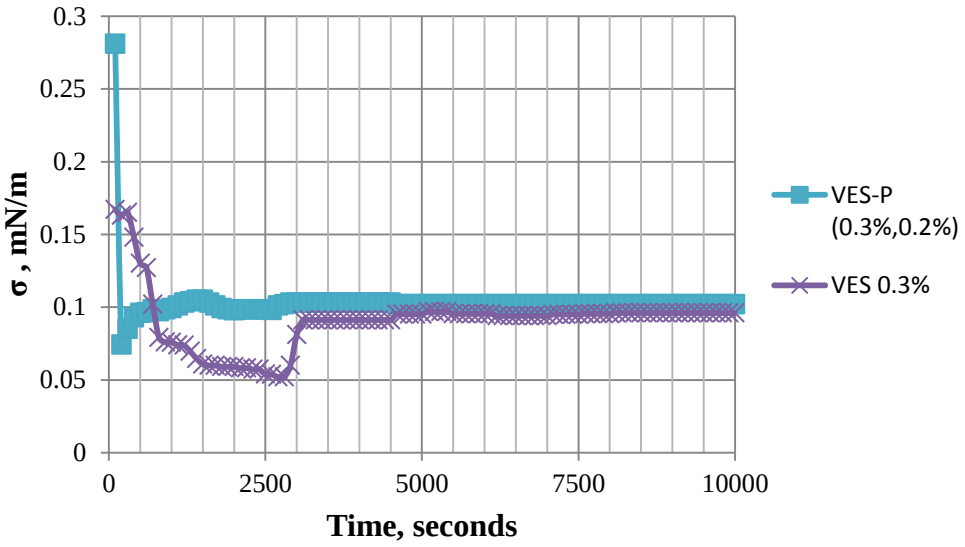


Figure 42: Effect of adding polymer to VES on its IFT

5.2.5 Effect of temperature on VES and S/VES

The **Figure 43** depicts the trend associated with VES and S/VES system upon the temperature increase from 30℃ to 70℃. The salinity was 57,000 ppm. The concentration of VES was 0.1 %. The concentration of S/VES was 0.2% (0.1% VES, 0.1% S). It is noticeable that VES system gives lower IFT than S/VES system over range of temperature. It has been discussed in section 5.2.3. However, an interesting trend is observed that though VES as a single system gives the non-linear trend with temperature, S/VES system gives linearly decreasing IFT with increasing temperature. For S/VES system, the IFT goes down with temperature because at higher temperature the IFT usually goes down for the surfactant due to weakening of the intermolecular force at the oil/surfactant solution interface (Aoudia, Al-Shibli et al. 2006). Also it is evident that when conventional surfactant is added to VES, its domination is higher over VES that it suppresses the shear viscosity of VES completely as it is discussed in section 5.3.3.2. Hence Surfactant behavior becomes dominant and restricted the S/VES system to shoot its IFT with increasing temperature unlike VES system. VES as single system gives higher IFT at higher temperature. As discussed in section 5.2.2, at higher temperature, entanglement might have induced, creating little solidity, thus it might have had interfacial viscosity and hence IFT goes up for VES alone system. Interfacial viscosity induces slower micellar activity. This could be the reason why VES generally are not ultra-low IFT agents. Added surfactant is the anti WLM agent which is discussed in section 5.3.3 and the reservoir that doesn't need mobility control could have S/VES systems as an option.

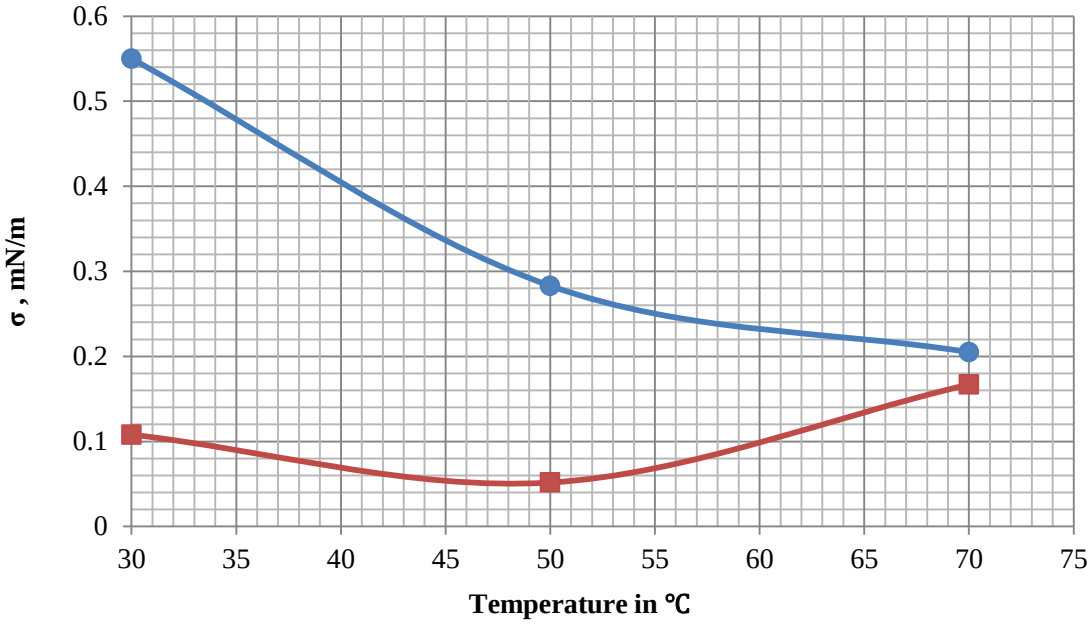


Figure 43: Effect of temperature on VES and S/VES

5.2.6 Effect of Aging on optimum VES

EOR is a process belonging to the long time scale which needs holistic planning. Though IFT reduction through VES is evident from the above discussions, its potentiality as an EOR fluid can only be assured if it is retaining its property on a longer scale. The aging was done for 3 months at 65℃. The salinity of the solution was 57,000 ppm and the concentration was 1%. The test duration was 10,000 seconds. The **Figure 44** illustrates the negative effect of aging on the IFT. VES 1% which initially gives the IFT of 0.047 m$\frac{N}{m}$ gives the IFT of 0.201 m$\frac{N}{m}$ at sustained aging for 3 months. Though the IFT of 0.201 m$\frac{N}{m}$ can mobilize the oil with little efficacy, its prospect as an EOR fluid can be advocated or proposed strongly if the IFT increment is mitigated. So we formulated the VES/R system which is discussed in detail in section 5.4.3.2.

5.2.7 Comparison of unaged VES, aged VES and VES/R systems

Having found the negative influence of aging over IFT reduction capability of VES, VES/R system was formulated by adding 0.1% of reducing agent to 1% VES. VES/R and VES systems were aged at 65℃ for 3 months. The systems were compared by carrying out the experiments at 50℃ and 57,000 ppm. The **Figure 45** clearly depicts the potential of reducing agent in mitigating the aging problems for an EOR fluid. IFT of aged VES and aged VES/R system are 0.201mN/m and 0.058mN/m. The reason behind this excellent combative behavior of VES/R system is due to its ability to optimize the susceptible portion of VES that are prone to oxidation. It is elaborately detailed on the molecular level in section 5.4.3.2 titled thermal stability optimization.

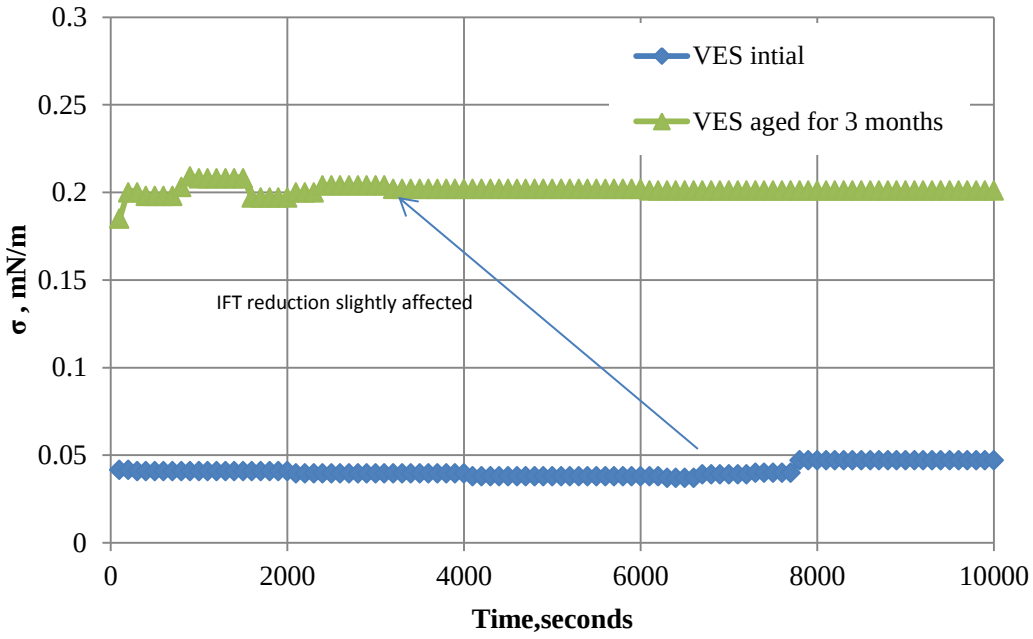


Figure 44: Effect of aging on the IFT of VES system

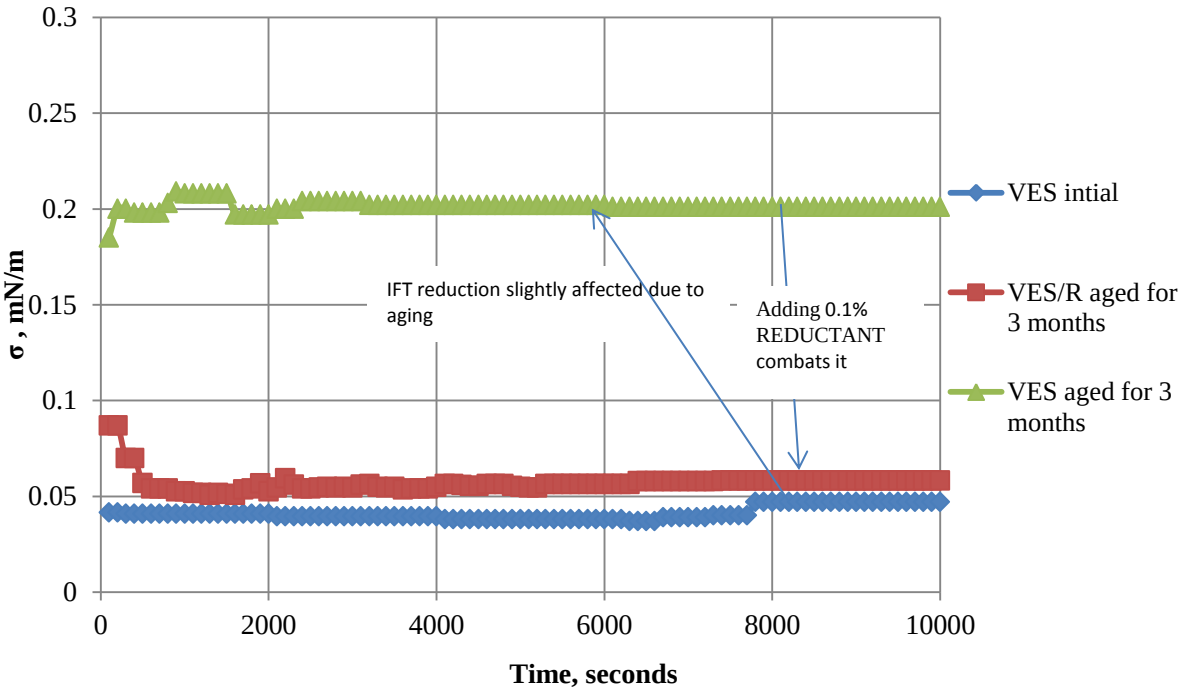


Figure 45: Comparison of IFT between unaged VES, aged VES and VES/R systems

5.3 Oil Recovery potential of VES, S/VES and VES/P system

This section starts with sub-section 5.3.1 stressing the importance of viscosity, IFT reduction in EOR perspective. Three different systems were studied for its viscosity/IFT ratio. It includes the VES system, S/VES systems and VES/P systems. VES system is considered as a replacement to both surfactant and polymer in Surfactant polymer flooding. In S/VES systems, VES is considered as a replacement to polymer in Surfactant polymer flooding. In VES/P systems, VES is considered as the replacement to surfactant in SP flooding. However their potential to replace conventional Surfactant polymer flooding in carbonate reservoirs lies on its ability to provide macroscopic sweep and microscopic displacement at the harsh conditions. Hence considering Viscosity/IFT ratio as the yardstick, the different combination of these systems was studied for its oil recovery potential.

Viscosity/IFT ratio of VES system at three different temperatures is presented in section 5.3.2. Viscosity/ IFT ratio of four different S/VES systems at 50℃ are presented in section 5.3.3. The optimum S/VES system was chosen from the four S/VES systems. The optimum S/VES systems were studied for its viscosity/IFT ratio at 70℃. The results are presented in section 5.3.3.3. The effect of changing the concentration of VES on the viscosity/IFT ratio of optimum S/VES was also studied and presented in section 5.3.3.4. Viscosity/IFT ratio of different combination of VES/P systems at 70℃ is presented in section 5.3.4.

Finally, to choose the optimum system among the VES, S/VES and VES/P systems, the Viscosity/IFT ratio of all the systems at the salinity of 57,000 ppm and at the temperature of 70℃ are tabulated and compared in section 5.3.5. The main objective of this

comparison is to choose the optimum system for recommending to the core flooding experiment which is discussed in section 5.5. The methodology sections 3.3.1, 3.3.3, 3.3.4, 3.3.5, 3.5, 3.6 details the solutions preparatory procedures, equipment and test procedure used in carrying out these studies.

5.3.1 Importance of viscosity, IFT and viscosity/IFT ratio for an EOR fluid:

5.3.1.1 Importance of viscosity for an EOR fluid:

Viscosity: Viscosity is the measurement of resistance to flow of liquid under shear stress. In EOR, viscosity of injection fluids is essential to

1. Provide higher sweep efficiency
2. Controlled mobility ratio
3. Avoid channeling
4. Avoid fingering

Volumetric Sweep efficiency (E_V): It is be defined as ratio of pore volume that has been contacted by the injected fluids to the total pore volume of the reservoir (Green and Willhite 1998). It is the viscosity which determines how efficiently the injection fluids sweep the oil in the reservoirs. As the viscosity is high, it tends to move slowly and uniformly contacting as much as pore volume. Volumetric sweep efficiency can be further divided into areal sweep efficiency and vertical sweep efficiency.

Mobility ratio (M.R): As discussed already section 1.5, it is the ratio of mobility of the injection fluids to the mobility of the residential oil (Green and Willhite 1998). Mobility ratio should be less than one to provide efficient sweep. Mobility is the ratio of effective permeability to the fluid viscosity. Adverse mobility ratio may lead to the early

breakthrough through either channeling via high permeable streaks and/ or fingering through high viscous oil.

Channeling: The tendency of the injected fluid to bypass through highly permeable streaks that are often saturated with water is called channeling. The injected EOR fluid should provide residual viscosity that would prevent the flow through streaks. Relative permeability to the oil should be increased, so that oil would be mobilized and water permeability would be reduced. IFT reduction is crucial here. VES has the special property that it could provide IFT reduction and also seeks oil zone and avoids water zone.

Viscous fingering: When a less viscous injection fluids is injected to displace more viscous oil, then it lead to instability in the form of penetrating fingers at the displacement front (Homsy 1987), (Sajjadi and Azaiez 2012). It is due to difference in viscosity. Hence it is essential for the injection fluid to possess high viscosity.

5.3.1.2 Importance of IFT reduction capacity for an EOR fluid:

IFT reduction**:** Interfacial tension is defined as the work which must be expended to increase the size of the interface between two adjacent phases which do not mix completely with one another. At a phase boundary, the sum of the interactions with the molecules of the same phase is greater than that of the interactions with molecules of the other phase. Accordingly, molecules at the interface have fewer attractive interacting partners than in the volume phase. The phases therefore form the smallest possible interface without the action of external force. Work must be done in order to increase the

size of the interface. Hence it exerts tension. The tension could be reduced through surfactants to enable the mobility of the trapped oil.

IFT reduction of an injection fluid is essential to

1. Reduce the capillary pressure
2. Reduce the residual oil saturation
3. Increase the displacement efficiency
4. Increase the relative permeability to oil

Capillary pressure (P_c): It is defined as the pressure difference between the two immiscible fluids in the reservoirs (Hyne 2014). It is caused by interfacial tension between them. Reducing the interfacial tension between oil and water with the aid of the surface active agents could reduce the capillary force that is trapping the oil.

Residual oil saturation (S_{or}): It is term used to denote the amount of immovable oil left behind after any recovery process. The amount of oil left behind after the secondary process is higher if the capillary pressure is higher (Sharma 2013). Higher capillary pressure at the tight portion of the reservoir say pore throat will not let the oil easily for movement. So IFT should be reduced first, that lowers the capillary pressure and hence facilitates mobilization

Displacement efficiency (E_D): Displacement efficiency is defined as the amount of oil that upon contacted is mobilized to the amount of oil that is not yet mobilized even after being swept. So displacement efficiency which is multiplicative of sweep efficiency

should be higher to get over all good recovery efficiency. IFT should be lowered, that reduces the trapping force and in turn it mobilizes and displaced the oil.

Relative permeability (K_{ro}): the ratio between the effective permeability of the oil at partial saturation to the absolute permeability of the fluid that has been 100% saturated with the fluid. Relative permeability is the function of the interfacial tension as more and more oil gets mobilized, relative permeability of oil goes higher and contributes to overall recovery of oil.

5.3.1.3 Importance of Viscosity/IFT ratio

Viscosity of an EOR fluid is important to provide higher viscous force that could control the mobility ratio and contact as much oil possible macroscopically both in vertical and areal direction. However, just contacting or sweeping the oil doesn't suffice as the oil is held by strong capillarity that it will not move and hence produced, unless the capillary force holding it is reduced microscopically. Higher IFT is leading to the higher capillary force. So an EOR fluid or slug should provide

a. lower IFT that could reduce the microscopic capillary force and
b. higher viscosity that could increase macroscopic viscous force

Hence considering viscosity/IFT ratio as the deterministic parameter, VES, S/VES and VES/P systems were studied separately in sections from 5.3.2 to 5.3.4 and best among them is chosen by comparison in section 5.3.5.

5.3.2 VES systems

VES as a single fluid is studied for its IFT reduction capacity and mobility control. VES as the single fluid provides the distinct advantage of obviating the requirement of

multiple slug injections that are susceptible to chromatographic separation in the reservoirs at the harsh conditions.

5.3.2.1 IFT reduction of VES systems

IFT of VES at various concentrations were measured with the spinning drop Tensiometer at 30℃, 50℃ , 70℃. The viscosity of the oil at room temperature was 12 cP. The results are shown in the **Figures 46, 39 & 47** respectively. The effect of concentration on the IFT of VES at three different temperatures is almost of same trend **(Figure 46, Figure 39 and Figure 47).** The salinity was fixed at 57000 ppm. VES 0.5 wt. % at 70℃ reduces the IFT between oil and water to 0.09 m$\frac{N}{m}$. Increasing the concentration beyond 0.5 wt. % does not reduce the IFT significantly. Even though IFT is not that ultra-low, VES can still contribute to displacement mechanism via its viscoelastic normal force, shear thinning etc. (Brand, Hansch et al. 2014). VES exhibits better shear thinning nature than polymer. The IFT reduction values of VES is combined with shear viscosity values of VES at various concentrations ranging from 0.1 to 1% at 30℃, 50℃ and 70℃. Their ratios are tabulated in the **Table 10, Table 11 & Table 14** respectively.

5.3.2.2 Shear viscosity of VES system

Shear viscosity of VES systems was measured with the rheometer. Shear rate of 5/s was used and temperatures were 30℃, 50℃, 70℃. The results are shown in the **Figures 48, 49 & 17** respectively. The effect of concentration on the shear viscosity of VES at three different temperatures is of same trend (**Figure 48, Figure 49 and Figure 17).** The salinity is fixed at 57000 ppm. At higher concentration, the shear viscosity increases drastically. However, oil viscosity should also be accounted while choosing the optimum

concentration. VES self assembles to wormlike micelles. The harsh conditions of high temperature and high salinity in deed facilitate WLM growth which gives viscosity. VES gives higher viscosity with increasing salinity and temperature (Degré, Morvan et al. 2011). This favors its applicability as a mobility control agent in harsh carbonate reservoirs. Another advantage of using VES as a single system that are capable of providing both mobility control and IFT reduction is that it is preclude the need for multiple slugs. Using multiple slugs leads to chromatographic separation of it in the reservoirs, reducing the efficiency of the overall process (Li, Shi et al. 2009). The shear viscosity values of VES is combined with IFT reduction values of VES at various concentrations to formulate viscosity/IFT ratio and presented in the **Table 10, Table 11 & Table 14** respectively.

5.3.2.3 Viscosity/IFT ratio of VES

Shear viscosity and IFT of the VES at various concentrations and temperatures were presented in the previous sections. In this section, viscosity/IFT ratio of VES at various concentrations at 30℃, 50℃ and 70℃ are tabulated in the **Table 10, Table 11 & Table 14** respectively. Viscosity/IFT ratio increases with concentration at all the three temperature studied. Higher viscosity/IFT ratio at 50℃ is due to the enhanced IFT reduction at that temperature and has been discussed in the **section 5.2.2**

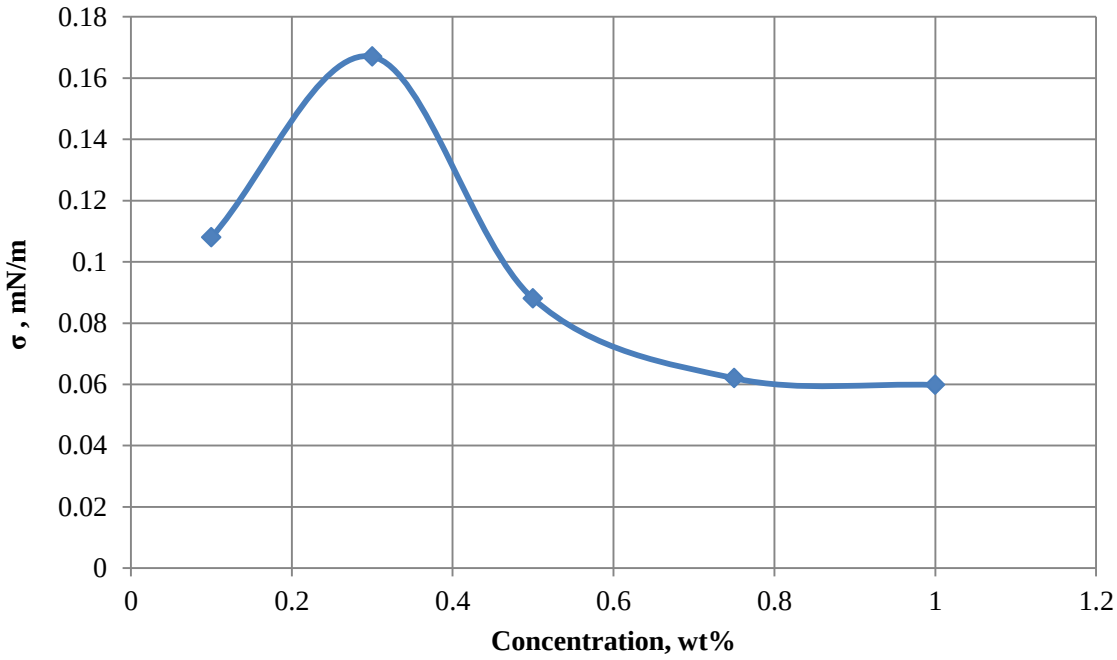


Figure 46: IFT vs concentration of VES system at 30℃

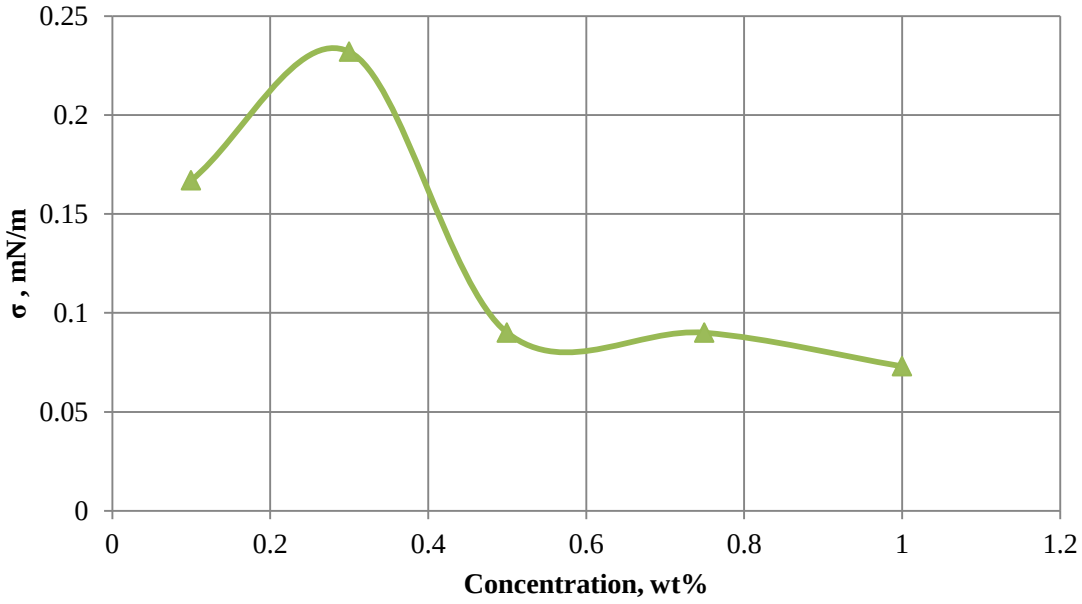


Figure 47: IFT vs concentration of VES system at 70℃

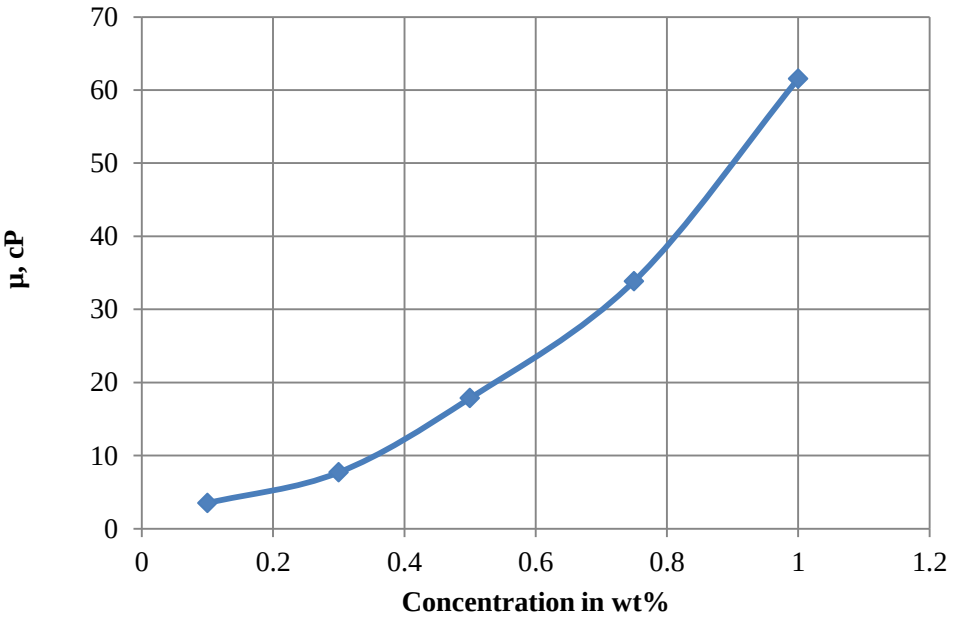


Figure 48: Shear viscosity vs concentration for VES system at 30℃

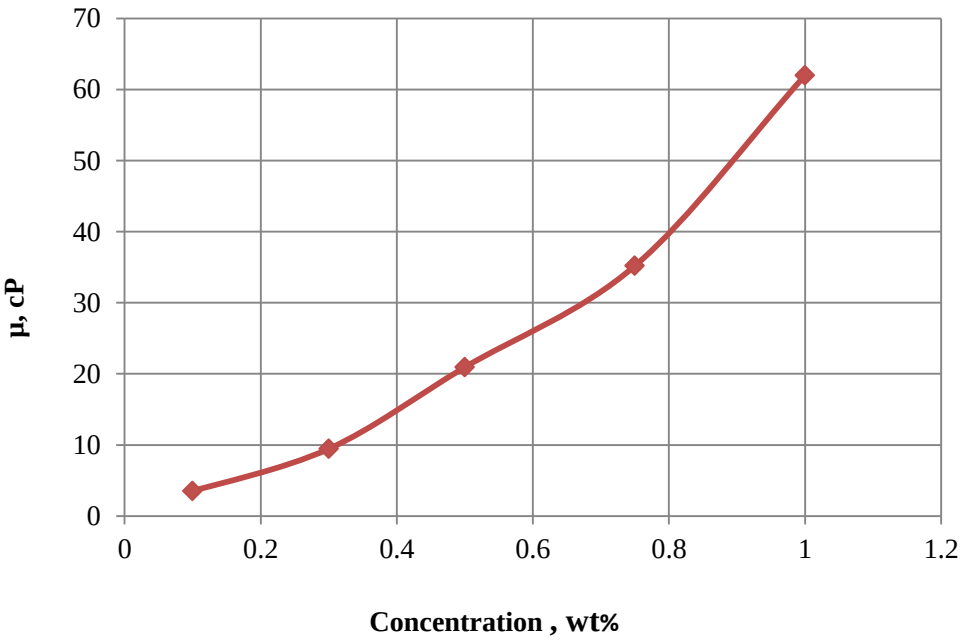


Figure 49: Shear viscosity vs concentration for VES system at 50℃

Table 10: Viscosity/IFT ratio of VES systems at 30℃

Concentration, wt.%	Viscosity, cP	IFT, mN/m	Viscosity/IFT ratio
0.1	3.5	0.108	32.40
0.3	7.7	0.167	46.10
0.5	17.85	0.088	202.84
0.75	33.86	0.062	546.12
1	61.56	0.0598	1029.43

Table 11: Viscosity/IFT ratio of VES system at 50℃

Concentration, wt.%	Viscosity, cP	IFT, mN/m	Viscosity/IFT ratio
0.1	3.5	0.0517	67.69
0.3	9.44	0.096	98.33
0.5	20.93	0.047	445.31
0.75	35.2	0.043	818.60
1	62	0.04	1550

5.3.3 S/VES systems

The effect of adding conventional surfactant to VES was investigated. In S/VES system, VES was considered more of the polymer. Adding conventional surfactant to VES might give lower ultra IFT. The effect of surfactant addition to VES on mobility control was also studied. Hence Cationic, anionic, zwitterionic and non-ionic surfactants (0.1 wt. % each) were added with VES 0.1 wt. % to formulate S/VES systems. IFT reduction and viscosity generation were studied.

5.3.3.1 IFT reduction by S/VES systems

IFT of 4 different S/VES system and single VES system was measured with the spinning drop Tensiometer at 50℃ . Oil viscosity was 12 cP. The salinity was 57000 ppm. The concentration of S/VES system was 0.2% and VES system was 0.1%. From the **Figure 50,** it is understood that adding conventional surfactant irrespective of the classes to VES

impacts its performance negatively. VES as a single system gives the lower IFT than 4 different S/VES system. It could be attributed that the conventional surfactant hampers the structure of VES completely. VES which worked well with added salts, fails with the additional conventional surfactants implies that salts which screen the electrostatic repulsion between the head groups are only needed for inducing viscoelasticity. Combination of different surfactants may induce viscoelasticity between the combining surfactant species (Raghavan, Fritz et al. 2002). However this is the parental VES that any other surfactant being added affects the packing parameter and hampers the overall property. Surfactants added to the already existing VES alter the structure of head and tail at a molecular level thereby making it ineffective. WLM may get converted into spherical micelles that could not as effective as WLM in terms of providing mobilization and mobility control. Added surfactant dominates the VES in S/VES system as evidenced in next section 5.3.3.2

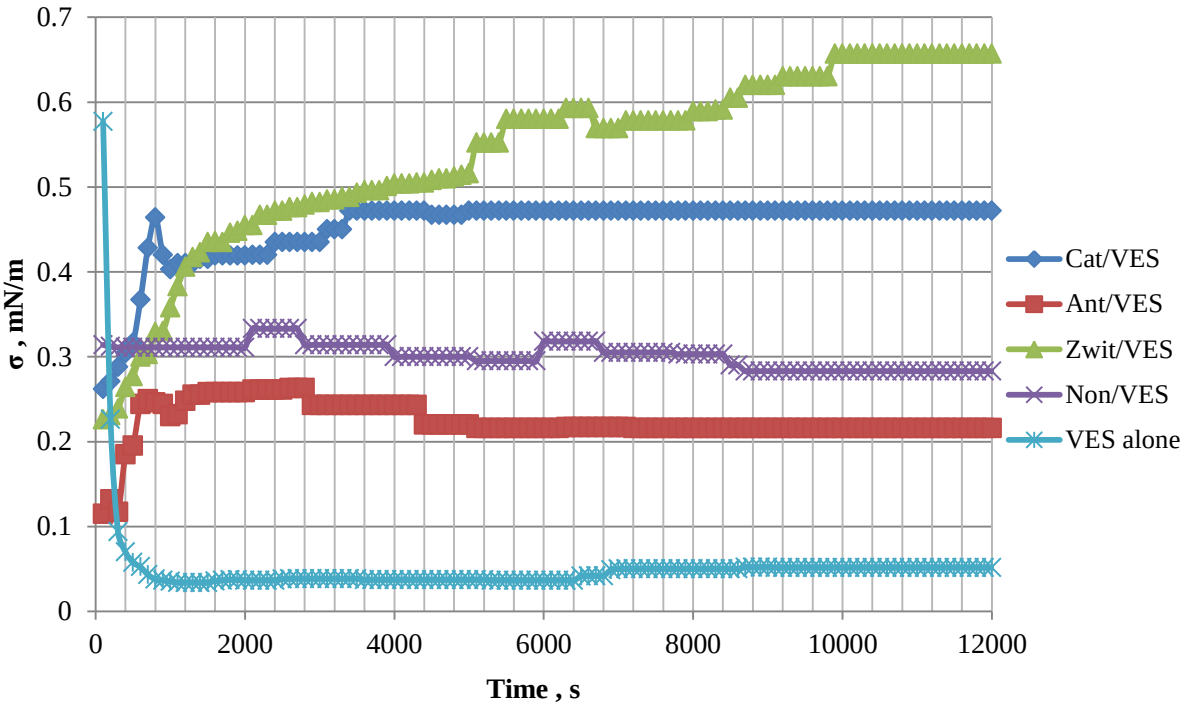


Figure 50: IFT of different S/VES systems at 50℃

5.3.3.2 Shear viscosity of S/VES systems

Shear viscosity of four different S/VES system was measured with the Rheometer. Shear rate of 5/s was used and temperature was 50℃. Shear viscosity of VES 0.1 wt. % was also studied for comparison **(Table 12).**

Table 12: Shear Viscosity of S/VES system at 50℃

S/VES system	Viscosity (cP)
Cat/VES	1
Ant/VES	1
Non/VES	1
Zwit/ VES	1
VES	3.5

Viscosity of VES also gets affected because of adding conventional surfactants. Irrespective of the type of surfactant being added, WLM of VES gets affected resulting in a watery like fluid with the viscosity of 1 cP **(Table 12).** The reasons could be that added surfactants increase the area of separation between the head groups in parental VES. The surfactant tail group might have interacted with the head group and interfere in their network build up. Thus it might have converted the WLM to spherical micelles incapable of generating any viscosity. The Thus S/VES system which fails to give viscosity is not recommended for heterogeneous or heavy oil reservoirs where mobility control is crucial. In case, if WLM growth of VES is unwanted such as to prevent plugging in matrix, then S/VES can be considered anti-WLM agent. Also optimality in terms of mitigating the IFT shoot up due to this combination should be considered.

5.3.3.3 Non/VES system

Among the 4 different S/VES system, Ant/VES gives the lower IFT **(Figure 50).** However, Non/VES was chosen as the optimum S/VES system due to better

a. Better Compatibility of Non/VES over Ant/VES with 57,000 ppm sea water as shown in the **Figure 51.**
b. Possibility of higher adsorption of negatively charged anionic surfactant with positively charged carbonate rocks due to electrostatic attraction

Viscosity/IFT ratio of Non-VES system:

IFT and shear viscosity of Non-VES system at 70℃ were 0.205mN/m and 1 cP and it is reported in **Table 13**. Shear rate was 5/s and salinity was 57000 ppm. Adding conventional surfactants to parental VES hampers the WLM growth and made the solution watery. One cannot expect VES to behave as a mobility control agent in S/VES system especially for the parental VES.

5.3.3.4 Does high concentration of VES improve the recovery potential of S/VES system?

Having analyzed the poor performance S/VES systems in terms of viscosity and IFT with 0.1% of non-ionic surfactant and 0.1% of VES, a study had been conducted by increasing the concentration of VES from 0.1% to 0.5%. With higher concentration, the VES's performance as the mobility control agent in S/VES system is studied.

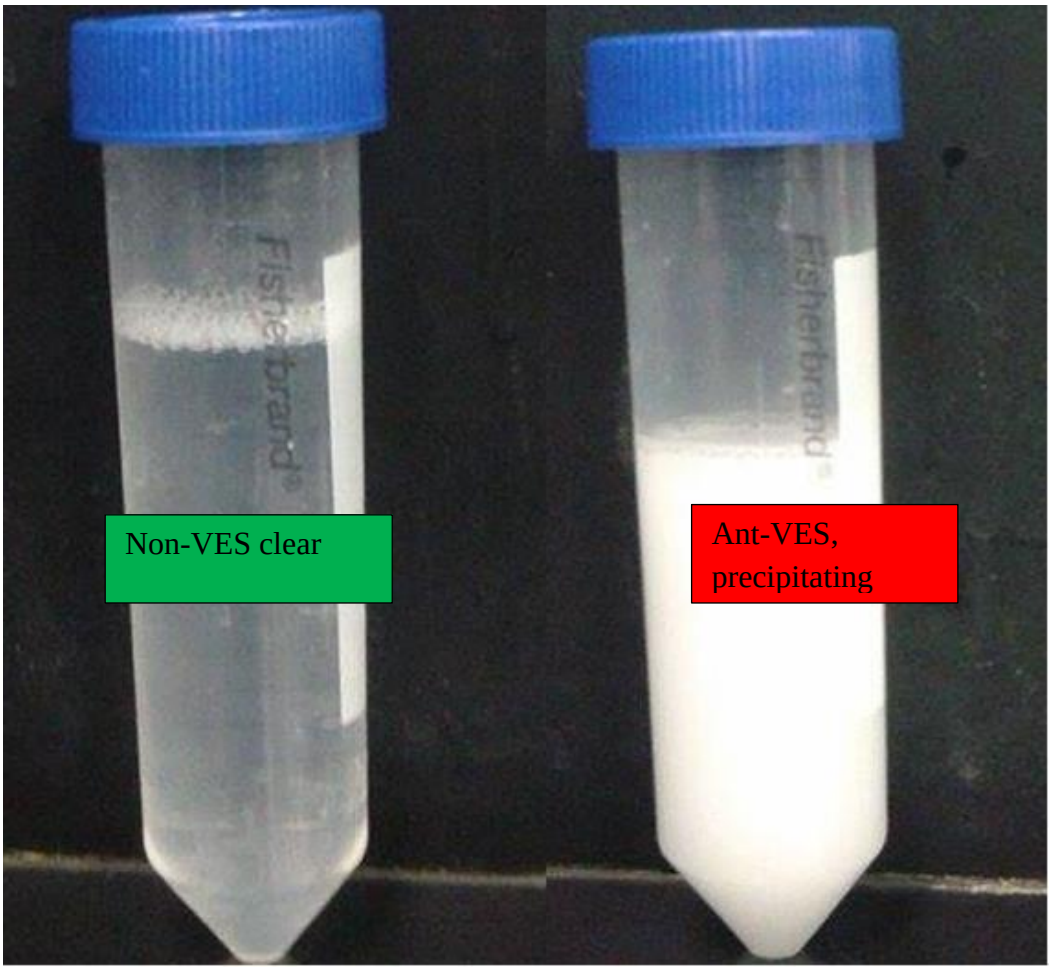


Figure 51: Compatibility of Non-VES and Ant-VES with 57,000 ppm sea water

The results attained through IFT and shear viscosity tests conducted at 70℃ and 57,000 ppm sea water are presented in the following **Table 13**. Shear rate of 5/s was used in measuring the shear viscosity.

Table 13: S/VES systems at different concentration

S/VES system concentration	Shear viscosity , cP	IFT , mN/m
0.1,0.1	1	0.205
0,0.1	3.5	0.167
0.1,0.5	1	0.138
0,0.5	22.6	0.09

VES inability to act as a mobility control agent in S/VES system remains the same irrespective of the concentration of VES used. Shear viscosity of 1 cP is attained while combing 0.5% and 0.1% of VES with 0.1% of surfactant. This clearly implies that the added conventional surfactant is strong inhibiter of WLM growth. IFT also gets affected because of the addition of surfactant to VES. IFT of 0.1% of VES shoots from 0.167 mN/m to 0.205 mN/m by the additional of 0.1% of non-ionic surfactant and IFT of 0.5% of VES of shoots up from 0.09mN/m to 0.138mN/m by the addition of 0.1% of conventional surfactant. The inability of VES even at higher concentration to behave as the mobility control agent in S/VES system in the presence of minute concentration of conventional surfactant implies that the conventional surfactant is too stronger than the parental VES and would be decisive in the behavior of the combinations. Combination of different surfactants to induce the WLM micelles at favorable conditions may require conventional surfactants. S/VES system could be a potential option in that scenario than

the one for parental VES studied in this research. It is strongly recommended to consider different combination of surfactants that could induce the formation of wormlike micelles at the conditions corresponding to the Middle East carbonate reservoirs.

5.3.4 VES/P systems

Micelles growth of VES can be arrested by its contact with oil (Berger and Berger 2008). It can be combated by adding polymer to VES forming VES/P system. Polymer provides the residual viscosity unperturbed by oil. Also polymer being cheaper than VES can reduce the cost of the formulation. Polymer's inaccessible pore volume might lead to chromatographic separation of polymer and surfactant. Polymer may flow ahead and could get adsorbed in the competitive adsorption process (Sheng 2010). Thus adsorption sites could be reduced for VES. VES/P system is formulated by different combination and concentration of VES and polymer to study the cost effective optimum Viscosity/IFT ratio. VES/P systems can be perceived as the SP system in which the VES acts as the surfactant.

5.3.4.1 IFT reduction by VES/P systems

IFT reduction of VES/P system was studied at 70℃. IFT of VES and P systems were also compared with VES/P formulations. The salinity was 57000 ppm and the concentration includes VES/P (0.4%, 0.1%), VES/P (0.1%, 0.4%), VES (0.5%), and P (0.5%).

From the **Figure 52**, it is clear that adding VES to polymer decreases its IFT reduction capability slightly. Adding polymer to VES increases its IFT which could be due to the interfacial viscosity increment that reduces the efficiency of oil mobilization. Hydrophilic polymer might have got intruded into the micelles thereby diminishing the micellar

activity **(Figure 29).** Further, VES/P system with higher polymer concentration (0.1%, 0.4%) gives slightly higher IFT when compared with the VES/P system of lower polymer concentration (0.4%, 0.1%). This again could be attributed to the intense anchoring of high concentrated polymer molecules into the micelles.

5.3.4.2 Shear viscosity of VES/P systems:

Shear viscosity of VES/P, VES and P system was studied at 70℃ at the shear rate of 5/s. Four systems that were studied for their IFT reduction were subjected to shear viscosity tests. The results are shown in the **Figure 53**. Viscosity/IFT ratio of each system is reported individually in **Table 14.** It is clear from **Figure 53,** that polymer undergoes thermal degradation from 30°C to70°C. VES viscosify with temperature. VES/P system with higher concentration of polymer undergoes follows polymer trend with intense thermal degradation while with higher VES concentration exhibit mild degradation. This could be due to the better thermal stability of VES than polymer (Degré, Morvan et al. 2011) .Further it is to be noted that VES gives lower shear viscosity than polymer. It has been reported in literatures (Morvan, Degre et al. 2012). Over all from VES/P systems, it is understood that for polymer flooding, adding a small concentration of VES may improve the displacement efficiency by mobilizing the residual oil owing to its IFT reduction capacity. For surfactant flooding, adding a small concentration of polymer may improve the sweep efficiency at the cost of slightly higher IFT or mildly diminished displacement efficiency microscopically. High viscous oil needs higher viscosity and low viscous oil in low permeable reservoir requires high IFT reduction capacity. Considering this, a comparison has been made between the all the studied systems for its recovery potential in the next section 5.3.5.

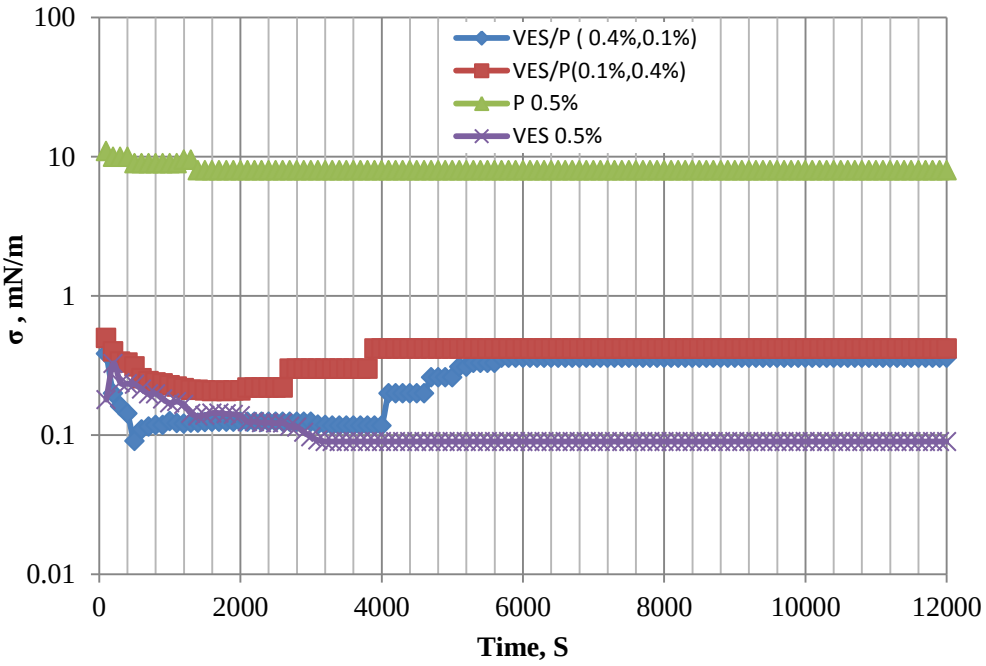


Figure 52: IFT of VES/P systems at 70℃

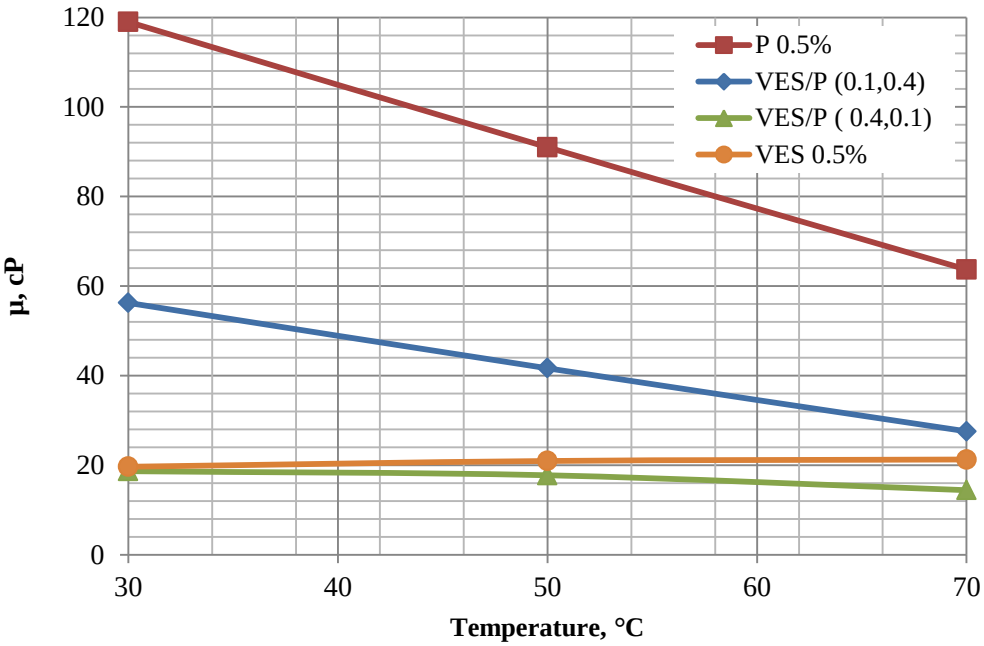


Figure 53: Shear viscosity of VES/P systems at 70℃

5.3.5 Viscosity/IFT ratio of VES, S/VES, P and VES/P systems at 70℃

In this section, the potential of VES, S/VES and VES/P in terms of viscosity/IFT ratio are compared. The purpose of chemical EOR process is to displace the residual or left behind oil by means of injection fluids. Efficiency of EOR can be written as multiple of microscopic displacement efficiency and macroscopic sweep efficiency. Microscopic displacement efficiency is the fraction of the oil that has been displaced from the swept zone. Macroscopic sweep efficiency is the fraction of the area contacted by injected fluid to the total contactable area. The IFT reduction by employing the surfactant improves the microscopic displacement efficiency. Viscosity generation by employing the polymer improves the sweep efficiency. Thus IFT and viscosity are the main parameters controlling the chemical EOR processes. The dimensionless Capillary number (Nc) defined as the ratio of viscous force to capillary force incorporates viscosity and IFT along with velocity and wettability angle (Green and Willhite 1998). Capillary number increment results in lowering of residual oil saturation. Capillary number increment is achieved by

a. increasing the viscosity of injection fluid to increase the sweep efficiency (using polymers)
b. decreasing the IFT between water and oil to increase the microscopic displacement efficiency or oil relative permeability (using surfactant)
c. decreasing the IFT and increasing the viscosity (using Viscoelastic Surfactant)

$\frac{Viscosisty}{IFT}$ Ratio (the raw form of capillary number without velocity term) could be used for convenience for characterizing the fluid ability in sweeping and mobilizing the oil.

Shear viscosities, IFT of various combinations of systems with 57000 ppm brine at 70°C reported earlier throughout sections 5.3.2 to 5.3.4 are summarized in **Table 14**. Shear rate of 5/s was used while measuring the shear viscosity.

Table 14: Summarized Viscosity/IFT ratio of various systems at 70°C

Systems	Concentration, wt.%	Shear Viscosity, Cp	IFT (mN/m)	$\frac{Viscosisty}{IFT}$
VES	0.1	3.5	0.167	20.95
VES	0.3	13.85	0.232	59.69
VES	0.5	21.26	0.09	236.22
VES	0.75	41.35	0.09	459.44
VES	1	74.66	0.073	1022.73
P	0.5	63.69	8	7.96
Non/VES	0.1,0.1	1	0.205	4.87
Non /VES	0.1,0.5	1	0.138	7.24
VES/P	0.1,0.4	27.55	0.42	65.59
VES/P	0.4,0.1	14.41	0.36	40.02

From the summarized **Table 14,** it is clear that Non/VES system screened as the optimum system from four different S/VES system is the failure just giving the viscosity/IFT ratio of just 4.87 for S/VES with the concentration of 0.1,0.1 and 7.24 with the concentration of 0.1,0.5. It is due to the arrestment of micelles growth of VES upon adding the conventional surfactant irrespective of the concentration of VES used. Polymer as a single system gives viscosity/IFT ratio of just 7.96. It is due to the inability of polymer to contribute to IFT reduction. Polymer interferes with the micellar activity of VES. It is

also clear that VES being a viscosifying surfactant is able to provide higher viscosity/IFT ratio than P, S/VES and VES/P system. It is mainly due to its ability in providing comparatively lower IFT. Hence VES could be used as a single fluid. Also, it has to be noted even though viscosity/IFT ratio is higher for higher concentration of VES; it is due to the higher viscosity generation because of entanglement (Chellamuthu and Rothstein 2008). VES 0.5% is the optimum as increasing the concentration beyond 0.5% doesn't reduce the IFT significantly as seen from **Figure 39.** Since the core flooding is to be done with the light oil and low permeable core, the emphasis is placed more on IFT reduction than viscosity and hence 0.5% is the optimum one both economically and potentially for recovery. Further VES/P (0.1, 0.4) also seems to be the option but at the expense of IFT increment associated with VES/P system over VES. Separation between VES and polymer is also a possibility. Though, it provides comparatively higher viscosity which is more important for mobility control**,** IFT lowering is much crucial in tight low permeable carbonate rocks. Hence VES as a single system is chosen as the optimum one for the low permeable tight carbonate core.

5.4 Thermal Characterization of VES

Though viscosity and IFT reduction are important for the recovery potential of EOR slugs, retaining those properties in hostile conditions for an extended period of time is essential. EOR is a full field process, unlike stimulation process. So thermal characterization of an EOR fluid should involve the tests that not only characterize the stability of the fluid on short term but also those that characterize their potential in retaining the properties associated with recovery potential on a long term in hostile conditions. Hence thermo gravimetric analysis and aging analysis were performed and

the results are presented in section 5.4.1 and 5.4.2. The methodology section 3.3.1, 3.3.3, 3.3.5 describes the solution preparation and the sections 3.9.1 and 3.9.2 describes the equipment and procedure used in carrying out TGA analysis and aging tests. Aging tests characterize the viscosity and IFT reduction capacity of VES on a long term scale. So shear viscosity and IFT measurements were measured as per the procedure stated in sections 3.5 and 3.6. Aging is done at several temperature to advocate the applicability of studied optimum VES as an EOR fluid to reservoirs of various temperature. Further, the optimization of thermal stability of VES is made by adding a reducing agent to it, thereby formulating Viscoelastic surfactant/ Reducing agent (VES/R) systems whose potential is also studied along with VES system comparatively at various temperature and the results are presented in section 5.4.3. As discussed in section 5.1.3, adding polymer to VES work synergistically because of polymer molecules intrusion in WLM. However to advocate it for EOR operations, their holistic assessment of its integral stability is crucial and VES/P systems were observed while aging for any separation between VES and polymer. Section 5.4.4 lists the oil field operations undertaken by Akzonobel so far and advocates the possible conversion of the VES from stimulation fluid to EOR fluid upon thermal optimization.

5.4.1 TGA Analysis

Thermo gravimetric analysis is used to the study the thermal degradation of different systems. Thermo gravimetric analysis was done on the VES, VES/P and P system using the procedure mentioned in section 3.9.1. VES, VES/P and P systems prepared with 57,000 ppm sea water were heated in the TGA instrument from 30℃ to 140℃. The concentration include 0.3% VES, 0.3% P and 0.3%VES, 0.2% P. This test carried out on

the short term just gives the over view of the stability of VES, VES/P and P systems. From the **Figure 54,** it is clear that after evaporation at 80℃, VES system maintained its stability from 80℃ to 140℃. However P and VES/P systems degrade until 110℃ signifying the polymer degradation. This is the short term testing more suited for evaluating the potential of well stimulation fluids. EOR fluid's thermal stability can only be confirmed through long term aging which is discussed in the following sections.

5.4.2 Aging

Aging refers to the process of heating the sample continuously at the higher temperature for longer period of time. This test is conducted to verify whether the VES, which is a sensitive living polymer, retains its WLM and maintains its mobility control effect. It is also conducted to verify the potential of VES/P systems at 85℃

5.4.2.1 Aging of optimum VES systems

The aging of VES 1% was done at 85℃ for 1 month. The section 3.3.1, 3.3.3, 3.3.5 describes the solutions preparatory procedure and section 3.9.2 describe the procedure used in carrying out these tests. The samples include Viscoelastic surfactant and polymer. Shear viscosity and IFT were measured initially, after 15 days and after 1month as per the procedures stated in sections 3.5 & 3.6. The **Figure 55** depicts the IFT changes upon aging the samples at 85℃. The experiment was carried out at 30℃ and the salinity was 57,000 ppm. The concentration of VES is 1 wt. %. It is clear that, the IFT keeps increasing with time which is not a good sign for an EOR fluid. IFT of VES after 1 month is 0.477 m$\frac{N}{m}$ which is almost 6 times higher than the initial IFT of 0.078 m$\frac{N}{m}$.

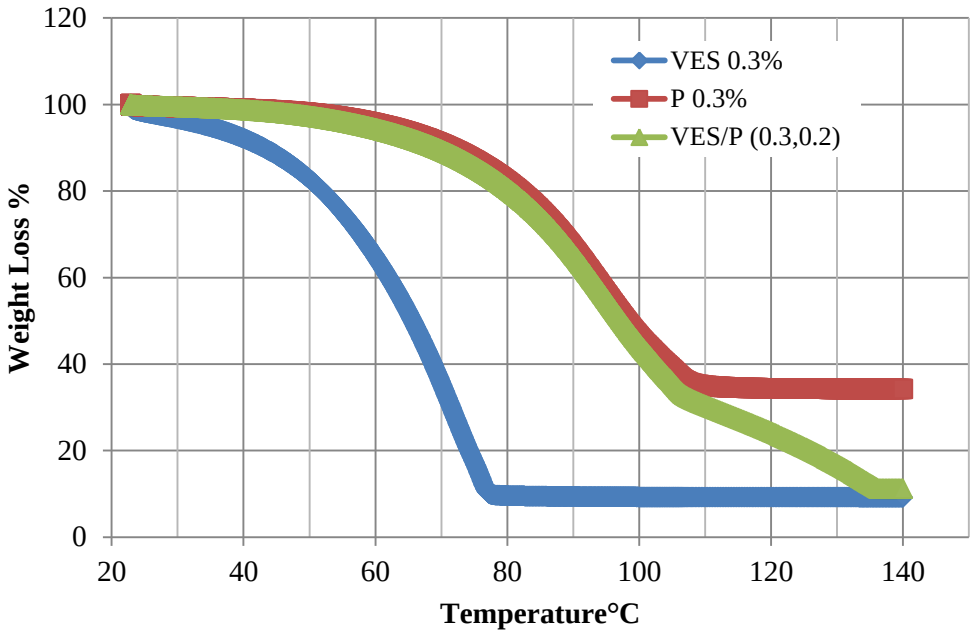


Figure 54: Thermal Degradation of VES, VES/P and P systems

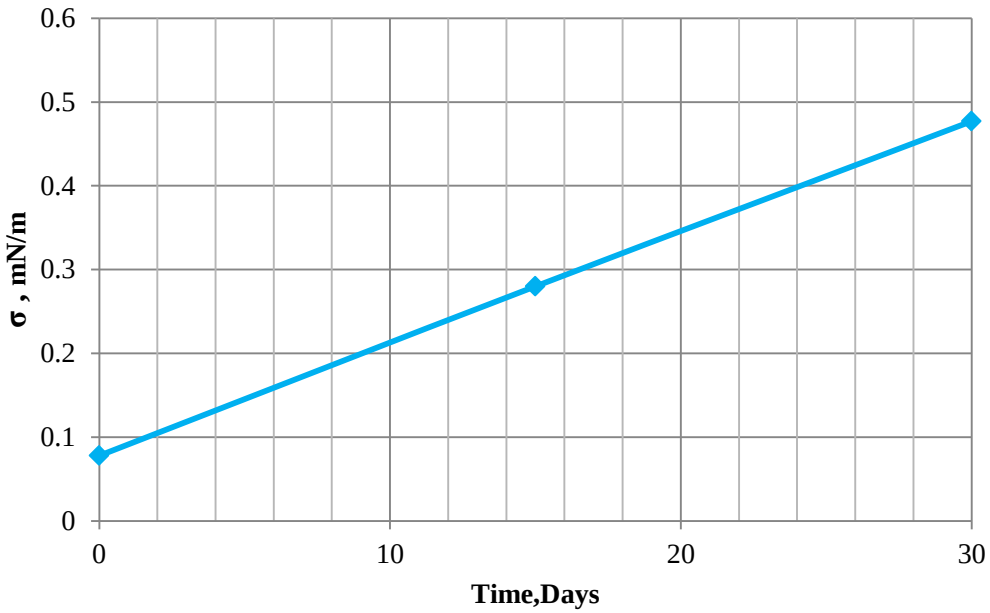


Figure 55: Effect of aging on the IFT of VES at 85℃

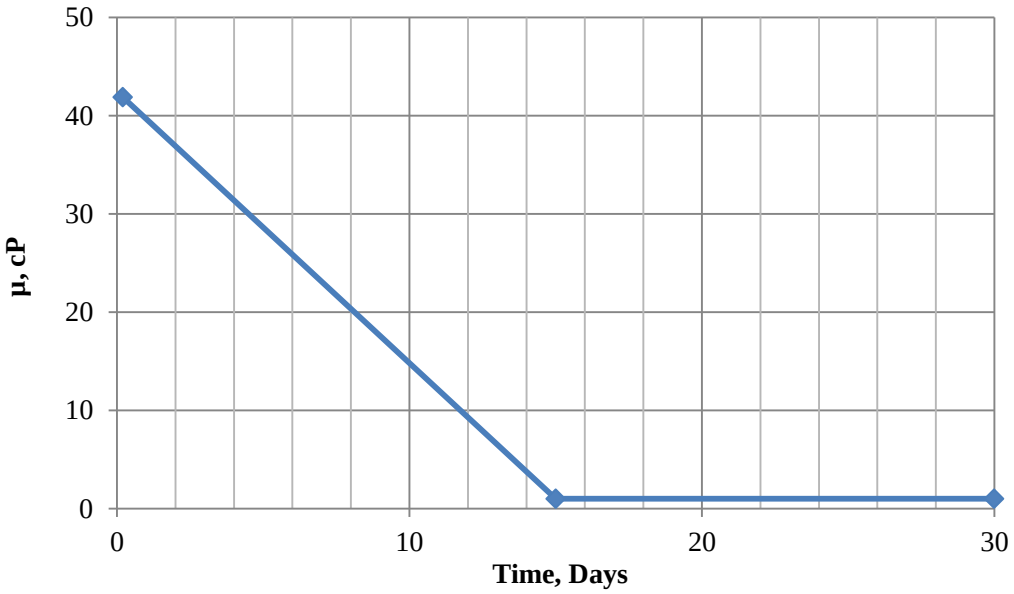


Figure 56: Effect of aging on the shear viscosity of VES at 85℃

With time, the potential of the EOR fluid's capability to mobilize the oil diminishes and hence could lead to ineffective displacement efficiency. For such fluids, the closer well spacing with higher injection rate is preferred. The fluids should be optimized to improve its IFT reduction capability as discussed in section 5.4.3 titled Improvement in thermal stability of VES.

The **Figure 56** depicts the effect of aging on the shear viscosity of VES system aged 85℃. Concentration of VES is 1 wt. %. The shear rate of 5/s was used. The measurement temperature is at 60℃. VES which gives the initial shear viscosity of 41.88 cP becomes watery after 1 month which is an indicative of the loss of WLM. Hence once the WLM is lost, it's potential as an EOR fluid is under scrutiny. One positive point that can be taken from this study is that continuous aging at higher temperature may be a sort of internal breaker for elastic VES that might be used as the diverting agent in fractured reservoirs as discussed in the section 5.1.5.5. However to consider VES as an EOR fluid , the long term stability at hostile conditions is mandatory and hence problems associated with it is identified and optimized which is discussed in section 5.4.3 titled Improvement in thermal stability of VES.

5.4.2.2 Aging of VES/P systems

VES/P system that was aged at 85℃ for 1 month was visually observed for any phase separation between VES and polymer at the hostile conditions. **The Figure 57** depicts the phase separation of VES and P during the continuous heating for 1 month of VES/P system at 57000 ppm salinity and at 85℃. It is due to breakage of WLM that the VES cannot hold any more the polymer that got adhered strongly as discussed in section 5.1.3.

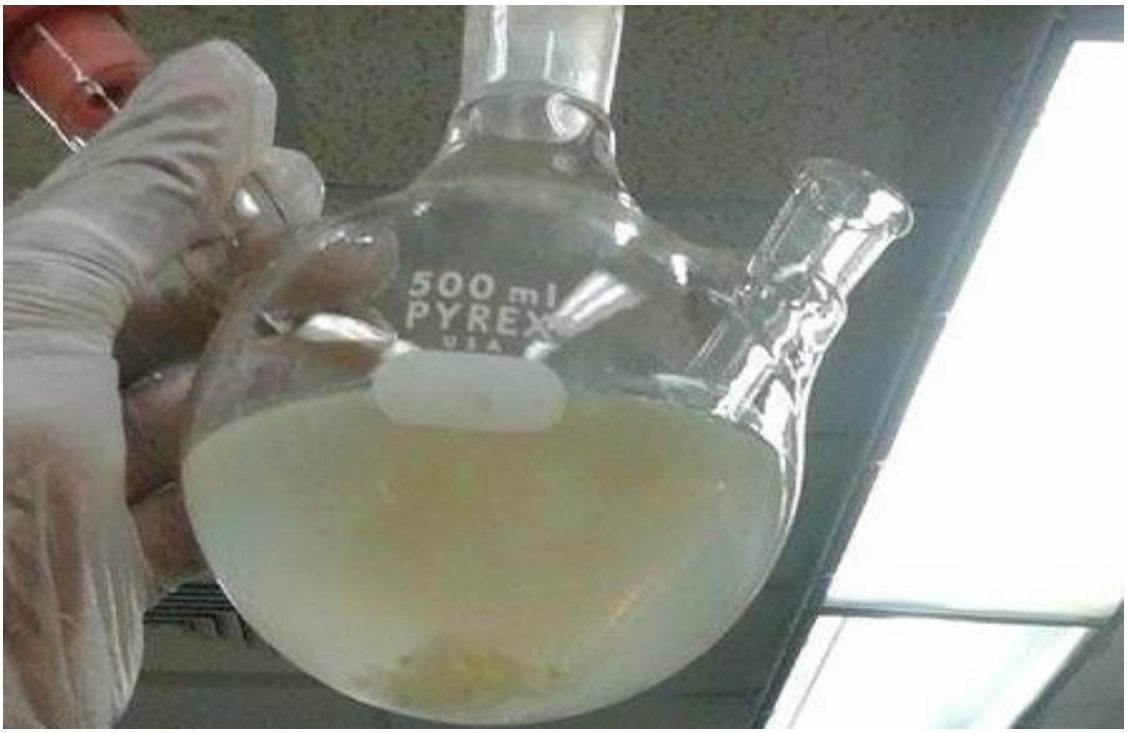


Figure 57: Visual observation of VES/P system aged at 85℃ for 1 month

5.4.3 Improvement in Thermal stability of VES (VES/R system)

From the previous discussion, it has been identified that VES which exhibits most of the favorable properties that an EOR fluid is supposed to possess fails to remain thermally stable at the hostile conditions for the longer time. Hence, in this section we studied the reason for its poor thermal stability and proposed a system called VES/R to combat the long term issues.

5.4.3.1 Why the performance of VES is poor?

Surfactant having both hydrophobic and hydrophilic moieties on the same molecule has the tendency to self-assemble into variety of structures. Surfactant forms WLM if it contains short hydrophilic head group and long hydrophobic tail groups. The head groups should be clustered together, for which the salts are essential to prevent electro static repulsion between them. Hence this is favorable for carbonate reservoirs containing high salinity. However certain carbonate reservoirs are also characterized by high temperature and EOR fluids should retain their displacement and sweep properties at those hostile temperatures for an extended time. Hydrophobic group contains unsaturated carbon-carbon double bond and hydrophilic group contains amide bonds (Chu, Feng et al. 2011). It is the long hydrophobic tails which gives lengthy micelles that entangles to give enormous viscosity. Dissolved oxygen oxidizes the unsaturated carbon-carbon double bond located in the hydrophobic tail at high temperature for a sustained period. Thus the tail gets affected and the micelle changes its structures from WLM to spherical micelles (Chu, Feng et al. 2011). They used amido sulfo betaine surfactant for the aging studies. The structure of amido sulfo betaine is shown in the **Figure 58.**

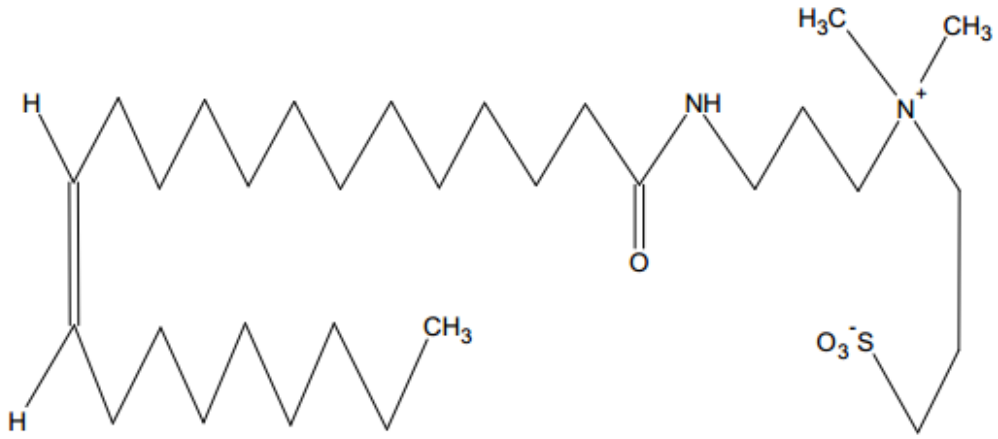


Figure 58: Structure of amido sulfo betaine

There exists the active carbon-carbon double bond in the hydrophobic tail and amido group in hydrophilic head as shown in the **Figure 58.** The solutions was subjected to aging for 60 days at 85℃ in the presence of 1% NaCl brine and it was inferred from rheological analysis that solution becomes watery. In the dynamic tests, the loss modulus is higher than the storage modulus. In the shear tests, it was observed that viscosity drops to the level of water. This is similar to the result obtained in our analysis as shown in **Figure 56.** It was perceived that the loss of WLM property is due to the breakage of unsaturated carbon-carbon double bond in the hydrophilic group due to the oxidation. It is confirmed through NMR analysis that head group of the amido sulfo betaine remain stable and the signals in the carbon-carbon double bond are weakened after the hostile aging. They used the reducing agent systems to combat it. The results were promising as both shear viscosity and storage modulus were retained in the presence of reducing agent.

5.4.3.2 Optimizing the thermal stability of optimum VES

The optimum VES used in our study also possess the similar structure to the one studied by (Chu, Feng et al. 2011) with unsaturated carbon-carbon double bond in the hydrophobic tail and amido group in the head. The VES commercially named as Armovis is Amide Tallow-(3-dimethyl amino) propyl), N-oxide. The general structure of Armovis is shown in the **Figure 59**.

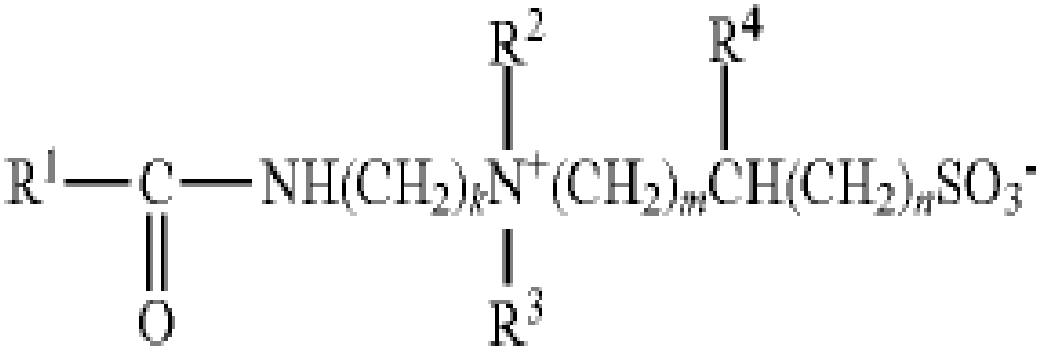


Figure 59: Structure of Armovis

Our component also has a very active unsaturated carbon-carbon double bond in hydrophobic tail and amido group in the hydrophilic head as shown in the **Figure 59**. The unsaturated region in the hydrophobic tail is susceptible to oxidation with the continuous hostile aging. Hence while aging at 85℃, it underwent oxidation, loses is WLM and resulted in the loss of dual function of IFT reduction and the coveted viscosity generation as shown in **Figure 56**.

How to improve?

Preserving the active unsaturated hydrophobic double bond in the tail from oxidation and promoting the tail growth is the way to improve it. Oxygen in the closed system should be exhausted to prevent oxidation that is prone at sustained high temperature in the most unstable part of the VES. (Chu, Feng et al. 2011) proposed the use of reducing agent to VES that could exhausts the dissolved oxygen and prevents the oxidation. Hence, 0.1% of reducing agent in the form of sodium trisulphate is added to VES forming VES/R systems. To ensure that the added reducing agent is not affecting the IFT, an unavoidable property, the aged sample is subjected to both viscosity and IFT tests. Aging is done at 65℃ and 95℃ Different aging temperatures are considered to evaluate the potential of VES to extend chemical EOR applicability to deeper reservoirs, moderate and high temperature reservoirs and even complicated heavy oil reservoirs. Further, thermally optimized results were also used to advocate the applicability of VES as an EOR fluid, thereby adding another horizon to the list of oil field operations provided by Akzonobel.

5.4.3.3 Aging of VES and VES/R systems at 65℃

VES and VES/R were the systems aged at 65℃. The concentration of VES was 1% and VES/R was 1, 0.1%. The salinity was 57,000 ppm. Oven is used for aging the samples for 3 months. The section 3.9.3.1 details the aging procedure associated with it. The IFT and shear viscosity were measured. The procedures used in measuring the shear viscosity and IFT are reported in section 3.5 and 3.6. The **Figure 60** depicts the effect of aging days on the IFT of VES and VES/R systems. The measurement temperature was 50℃. The VES system which gave the initial IFT of 0.047mN/m loses almost 75% of its reduction strength after 3 months by giving an IFT of 0.201mN/m. However adding 0.1% of reducing agent to the aged VES (VES/R system) gives the IFT of 0.0583mN/m which implies that almost 80% of the IFT reduction strength is maintained by preserving the unsaturated carbon-carbon double bond in the hydrophobic region from oxidation. This further indicates that oxidation through persistent aging not only deteriorates the solidity of VES, it also affects the interfacial property. VES/R system mitigates it.

The **Figure 61** depicts the effect of aging days on the shear viscosity of VES and VES/R systems. The shear rate of 5/s was used and the measurement temperature was 60℃. The VES system which gave the initial shear viscosity of 44.43 cP loses almost 40% of the viscosity after 3 month aging by just giving the shear viscosity of 25.87 cP. However adding 0.1% of reducing agent to the aged VES (VES/R system) gives the viscosity of 44.52 cP which implies that complete mobility control effect is retained. This strongly advocates the applicability of VES as an EOR fluid for high salinity and moderate temperature reservoirs by providing dual function of IFT reduction and viscosity generation obviating the need for multiple slugs prone to chromatographic separation.

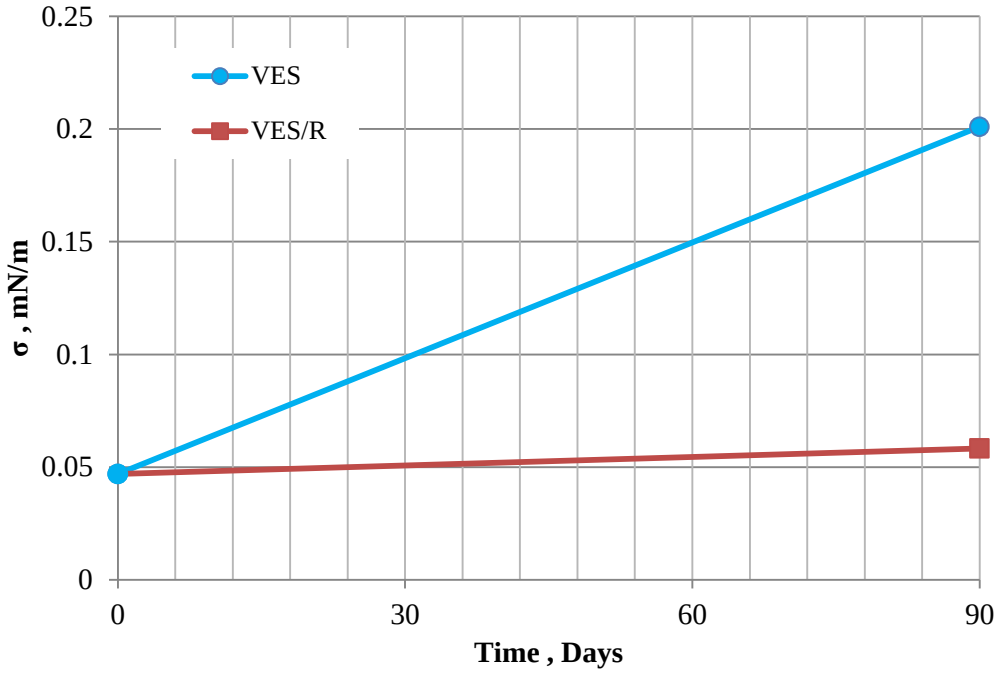


Figure 60: IFT vs aging time for VES and VES/R system at 65℃

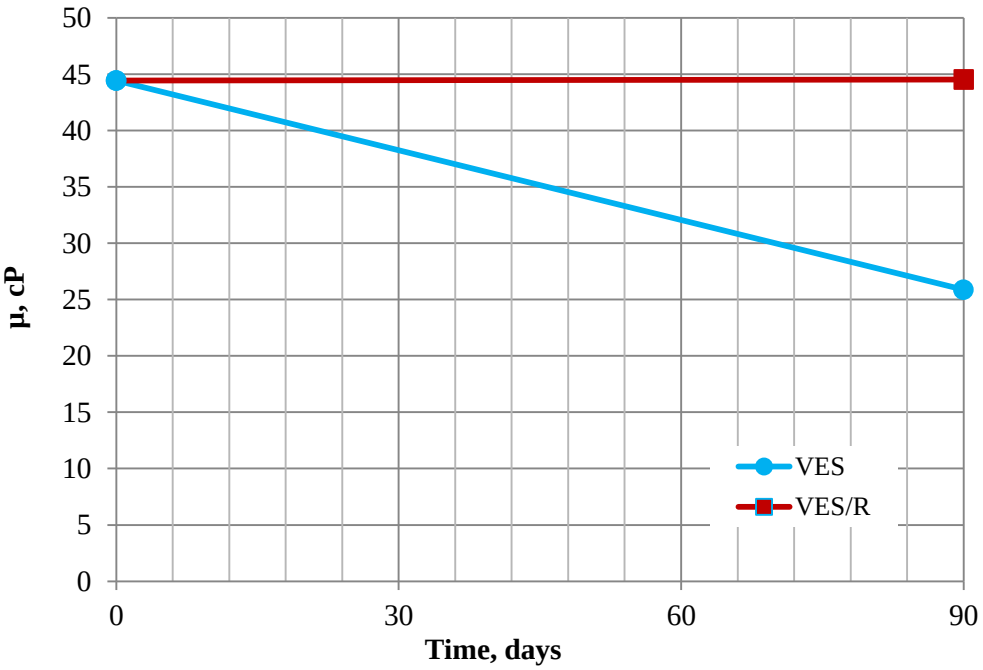


Figure 61: Shear viscosity vs aging time for VES and VES/R system at 65℃

5.4.3.4 Aging of VES and VES/R systems at 95℃

Results from aging at 65℃ confirm the positive potential of VES/R systems. Thus it could arguably be advocated that VES/R system can be a potential EOR slug for high salinity, moderate temperature reservoirs. However, reservoir temperature is still higher in some carbonate reservoirs and hence the test was carried out at 95℃. The procedure is detailed in section 3.9.3.2. VES system of 1% and VES/R system of 1%, 0.1% were used. Viscosity was measured with the viscometer and the procedure adopted in carrying it out described in section 3.8. The **Figure 62** depicts the effect of aging at 95℃ for 30 days on the viscosity of VES and VES/R systems. Viscosity measurements are done with Ostwald viscometer at room temperature. The initial viscosity of 19.06 cP attained with VES drops to 3.56 cP indicating that more than 80% of mobility control effect associated with VES is lost after 1 month hostile aging at the temperature of 95℃ and the salinity of 57000 ppm. However adding 0.1% of reducing agent to VES (VES/R system) reduces the viscosity to 14.85 cP thereby retaining almost 77% of the viscosity. Viscosity of VES/R system after 1 month of aging is 14.85 cP which is 4 times higher than 3.56 cP attained by poorly thermally stable VES system. Reducing agent mitigated the detrimental oxidation of VES in active, unsaturated, hydrophobic tail thereby retained its WLM and hence mobility control effect. This strongly states the adding reducing agent to optimum VES improves its thermal stability and expands its applicability from well stimulation fluid to prospective EOR fluid**.**

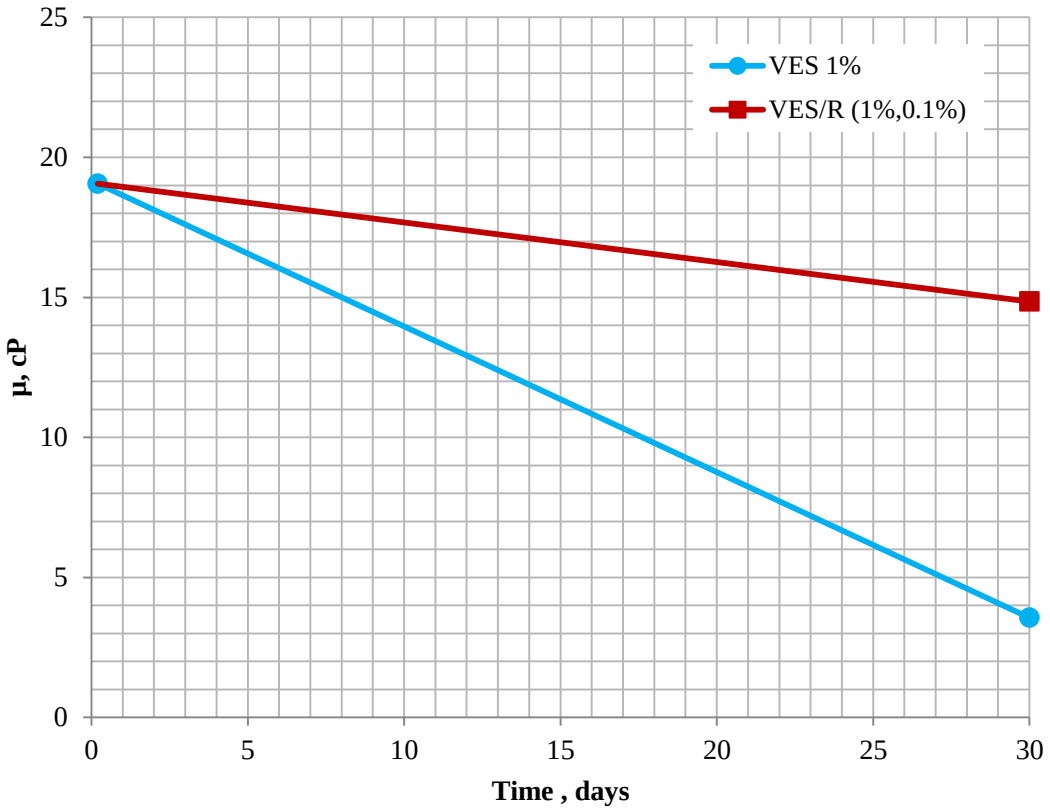


Figure 62: Viscosity of VES and VES/R systems aged at 95℃ for 1 month

5.4.4 Well stimulation's Fluid for EOR

Akzonobel had developed broad range of products for various oil field applications such as drilling, cementing, completion, production and stimulations. Traditionally used viscoelastic surfactants can viscosify up to 120℃ for well stimulation operations (Holt and Zhou, 2011). Optimum VES studied in this research is the most recent addition to viscoelastic surfactant products range from Akzonobel. Commercially called as Armovis, this optimum VES studied is capable of providing unsurpassed viscosification up to 180℃ for well stimulation process (Holt and Zhou, 2011). It is the most advanced well stimulation fluid developed by Akzonobel up to date. Well stimulation is a short term near well bore process. So the fluid successfully tested for its effectiveness as the well stimulation fluid may or may not be the potential one for long term full field EOR process. In deed it is not an effective EOR fluid especially in mobility control perspective particularly for high temperature applications as seen from **Figure 56**. The reasons are subsequently discussed in section 5.4.2.1. Even it has been reported by AkzoNobel, that viscosification of this particular VES degrades with time at higher temperature (Holt and Zhou, 2011). But the researchers of Akzonobel were contented with that limited thermal stability as they dealt with well stimulation. However EOR is more complex and demanding than well stimulation that not only requires higher capital and longer operational time but also shrewd optimization holistically. The astutely formulated VES/R system by analyzing its molecular structure improves its thermal stability on a longer run as seen from **Figures 60, 61 & 62** and discussed in sections 5.4.3.2, 5.4.3.3 and 5.4.3.4. So the studied thermally optimized optimum VES can be an effective EOR fluid for high salinity and high temperature carbonate reservoirs. Thus the studied VES,

originally a well stimulation fluid for carbonate reservoirs can be considered and advocated as an EOR fluid that too for harsh carbonate reservoirs. Apart from long term thermal stability, other properties such as shear viscosity, IFT reduction, shear thinning potential, reversible shear thinning, elasticity, positive influence towards high salinity; residual oil saturation reduction potential also favors this consideration as an EOR fluid for carbonate reservoirs. Further, having VES that provides the dual function of mobility control and mobilization enhancement obviate the need for multiple slugs that are prone to the chromatographic separation in the reservoirs. Thus EOR can also be added as one of the oil field operation that the Akzonobel developed VES can provide while optimizing it with the reducing agent as proposed by us in this research.

5.5 Core flooding

Core flooding was done on carbonate core at 80℃.It starts with core preparation, aging, permeability measurement, oil saturation, water flooding and VES flooding. VES 0.5%, identified as the optimum one from section 5.3.5, based on viscosity/IFT ratio was used for core flooding. The objective of the core flooding was used to determine the capability of VES in reducing the residual oil saturation/remaining oil saturation in the mature water flooded core. Hence there is no follow-up slug added to the main slug VES. The results involving permeability measurement, connate water saturation and flooding are presented in sections 5.5.1, 5.5.2 and 5.5.3 respectively. The detailed explanation about the water flooding and VES flooding is presented in section 5.5.3. The potential of the studied optimum VES and proprietary Wintershall's VES are compared in section 5.5.4. The potential of EOR using VES in carbonate reservoirs is compared with other EOR methods in section 5.5.5.

5.5.1 Permeability Measurement

Darcy law: The velocity of the homogeneous fluid in porous medium is directly to proportional to pressure gradient and inversely proportional to viscosity.

$v = \frac{q}{A} = \frac{k*dP}{\mu*L}$ …….. (8)

Where

$v =$ Velocity of fluid in $\frac{cm}{s}$

q = flow rate in $\frac{cm^3}{s}$

k is the absolute permeability in $Darcy$

d P is the differential pressure in $atmosphere$

μ is the viscosity of the injected fluid in cP

L is the length of the core in cm

A is cross sectional area in cm^2

$\frac{q}{dp} = m = \frac{A*k}{\mu*L}$…… (9)

$\frac{q}{dp}$ is the slope (m) to be determined

Determination of slope:

The formation water is flown at the 4 different rates and corresponding dP can be measured. It is reported in the **Table 15.** After converting into the appropriate units **(Table 15),** the slope is determined.

Table 15: Series of flow rate and corresponding pressure drop

Parameters	q, cc/min	q, cc/s	d P , psi	d P, atm
Values	1	0.016	7.8	0.536
Values	1.5	0.025	11	0.748
Values	2	0.033	14	0.952
Values	2.5	0.041	16.5	1.122

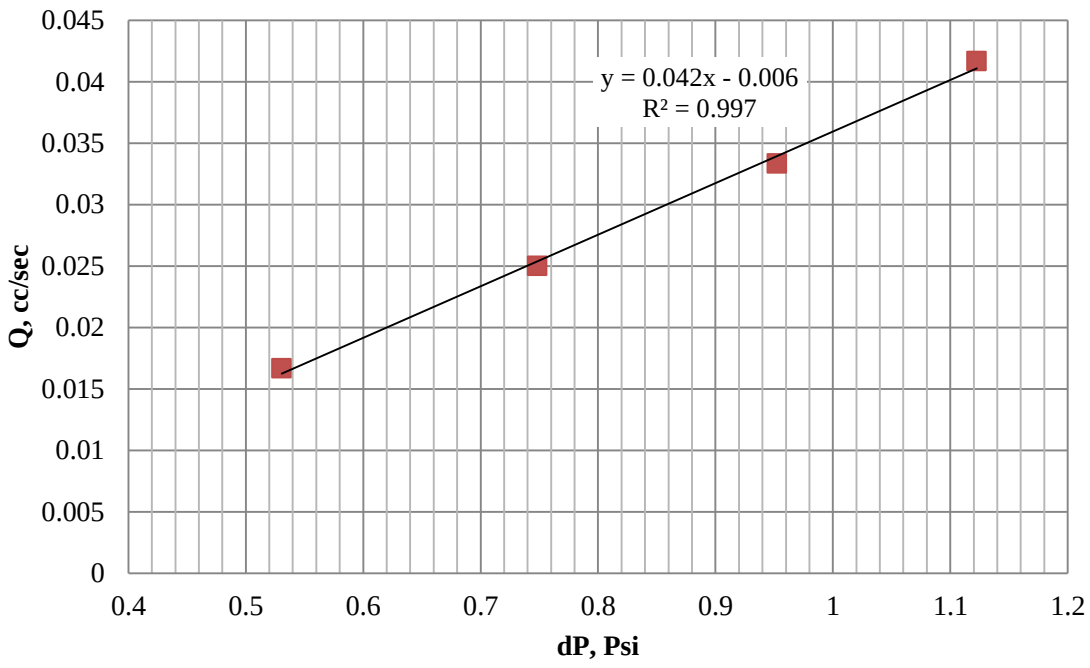


Figure 63: Determination of slope for measuring absolute permeability

The slope (m) is measured to be 0.042 from **Figure 63**. The slope obtained by plotting flow rate vs absolute permeability can replace the term $\frac{q}{dp}$ in the Darcy law. The diameter, cross section area, length of the core and the viscosity of formation water given below:

Diameter of the core = 3.8 cm.

Cross sectional area = $\left(\frac{3.14}{4}\right) * d^2$

Length of the core = 30.4 cm

Viscosity of water = 1 cP.

Upon substitution these parameters into equation (9)

$\frac{q}{dp} = 0.042 = \frac{\left(\frac{3.14}{4}\right)*d^2*k}{\mu*L}$ .....(10)

k = 113 milli Darcy.

It is the low permeable rock necessitating the need for reversible shear thinning for EOR fluids to undergo shear thinning to contact more area.

5.5.2 Connate Water Saturation (S_{wc})

It is essential to determine the connate water saturation to calculate initial oil in place.

Calculation of connate water saturations:

PV=69.19 ml

Total water recovered = 33+ 7+5= 45 ml

Water recovery factor= 45/69.19*100= 65.03% = 0.65

So connate water or irreducible water saturation = 0.35 or 35%

This implies almost 35% of the PV contains water that is immobile. So even if the reservoirs are preflushed with sea water of 57,000 ppm, a considerable amount of high salinity water remains. Being highly saline, it may deteriorate the performance of injection slugs. Care has to be taken to ensure the designed slugs not only resist sea water salinity, but also the formation water salinity level to some extent. Hence the shear viscosity of the VES with formation water and combined water is reported in section 5.1.4. The results were in favor of VES's potential in the worst possible scenario.

5.5.3 Water flooding followed by VES flooding

Having measured the permeability, connate water saturation, the core was subjected to aging at 80℃ for 15 days before flooding it with sea water of 57000 ppm and VES 0.5% until the residual oil saturation are obtained.

The reduction in residual oil saturation with respect to the pore volume injection of water flooding and VES is depicted in **Figure 64.** The increment in recovery factor with respect to the pore volume injection of water flooding and VES is depicted in **Figure 65.** The efficiency of water flooding is poor, that it could leave almost 65% of oil immobilized and unswept with 1.3 PV. Recovery factor of water flooding is just 35.23%. Water flooding continues up to 2 PV to ensure no oil is coming and to create the mature water flooded core. Hence this low permeable carbonate core is an ideal candidate to the study the efficacy of the VES as an EOR fluid.

The reasons for the poorer performance of water flooding in 113md permeable core could be attributed to the existence of higher capillary pressure. Low permeability results in higher capillary pressure (Guo, Ghalambor et al. 2004). Higher capillary pressure results in the higher capillary force and interfacial tension. Brine flooding with salts cannot reduce the interfacial tension to an appreciable level enough for mobilizing the oil. So, water flooding results in the poorer displacement efficiency. Also sweep efficiency cannot be 100% while flooding with low viscous water. It results in overall poor recovery efficiency leaving almost 65% of oil yet to be recovered in this low permeable, water flooded core.

VES 0.5% was chosen as the optimum system based on viscosity / IFT ratio **(Table 14)**. Though higher concentration of 0.75% and 1% gives higher viscosity/IFT ratio, considering the economics and viscosity of light oil, 0.5% was chosen as the optimum. VES 0.5% is injected at the rate of 24ml/hr. It is seen from the **Figure 64,** that VES could reduce the residual oil saturation from 0.421 to 0.23. It almost produces additional 30% of oil with just around 1.5 PV injections. This excellent recovery is due to dual function, shear thinning and viscoelasticity. Shear thinning is the property that aids the movement of VES into the low permeable zones. Low permeable zone should have exerted the pressure on the viscous VES molecules and VES responds to it by relieving the stress as discussed in section 5.1.1.4. It is seen from the **Figure 66** that the pressure drop increases in the wavering manner. It could be due to the shear thinning behavior of VES when it encounters a low permeable region. Reversible shear thinning property of VES discussed in section 5.1.2.2 should have resulted in the regeneration of viscosity and elasticity upon encountering the permeable or stress-free voidage region created by the release of

mobilized oil due to IFT reduction. So, the pressure drop though it is wavering it is increasing **(Figure 66).** VES is more viscous than oil. This ensure good sweep. Further VES provides the IFT reduction for mobilization as discussed in section 5.2.1. Shear viscosity ensures that mobility control is not affected as discussed in sections 5.1.1, 5.3.2.2. Elasticity also could have contributed to the recovery by dragging the left over oil in the low permeable region as discussed in section 5.1.5.2. Elasticity may increase the pressure drop **(Figure 66).** Injectivity would not be a problem as the fluid will get diverted and the pressure drop would get distributed due to the heterogeneity of the reservoir. Pressure drop would not be reaching the well head. VES as a single fluid providing both IFT reduction and viscosity generation performs efficiently throughout without risking any chromatographic issues commonly associated with multiple slugs. VES potential to retain viscosity with combined water should have maintained their sweep even in the zones saturated with connate formation water as discussed in section 5.1.4. All these recovery mechanism should have led to the excellent recovery. Another interesting mechanism that should have contributed to the recovery is the potential of VES to selectively seek the oil bearing zone as reported by (Berger et al., 2005). The potential of VES to loss its viscosity upon contacting oil in turn would help to penetrate the oil bearing zone selectively without sweeping the water zone. The schematic of selectively seeking oil bearing zone by VES reported in their work is depicted the **Figure 67**

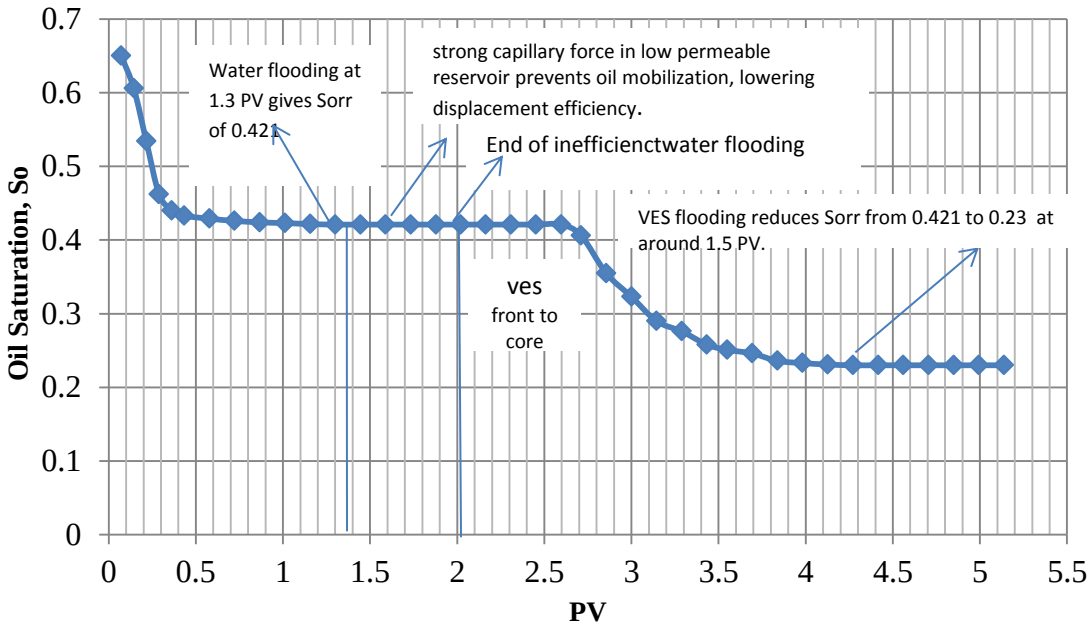


Figure 64: Residual oil saturation vs Pore volume during water flooding and VES flooding

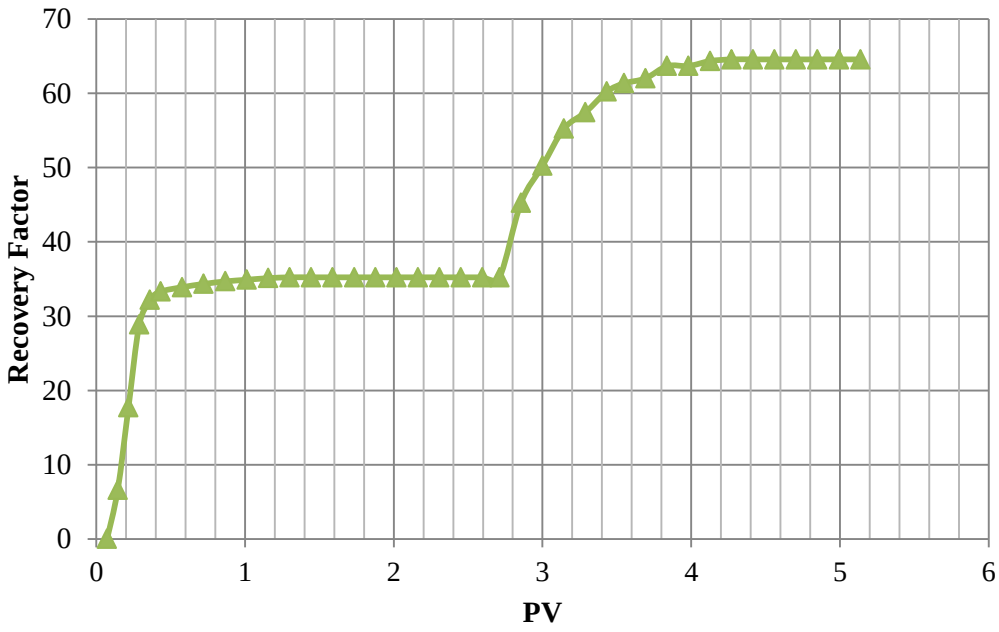


Figure 65: Recovery factor vs Pore Volume during water flooding and VES flooding

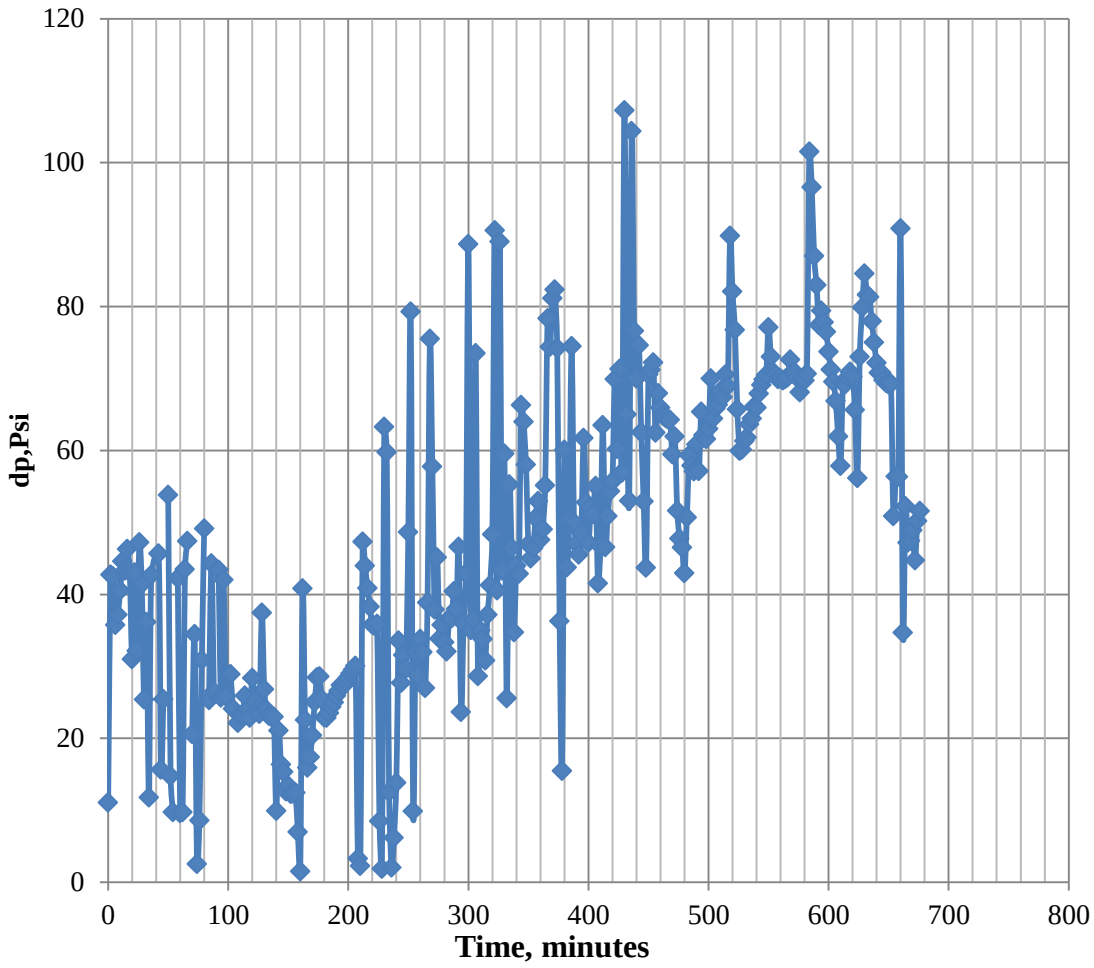
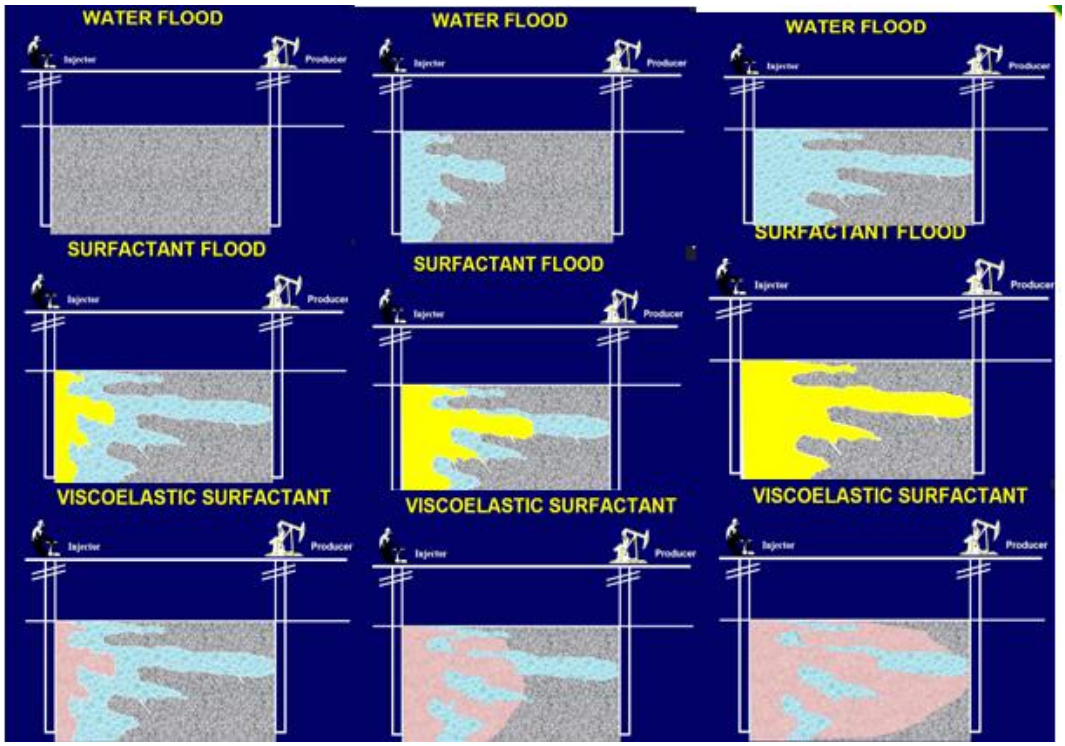


Figure 66: Pressure drop during water flooding and VES flooding



After Berger et al., 2008

Figure 67: Selective movement of VES to oil bearing zone

The **Figure 67** that depicts the schematic of water flooding, conventional surfactant floods and viscoelastic surfactant flooding clearly shows the additional area contacted by VES. It leads to higher sweep efficiency and conformance control which is of higher importance in heterogeneous carbonate reservoirs. It also shows that the conventional surfactant flooding just follows the water flooded path thereby could not contribute to any additional sweep efficiency. Surfactant as a single slug is not advisable for the reservoirs with higher heterogeneity and higher oil viscosity. Selective movement of surfactant may lead to channeling and fingering due to heterogeneity and high oil viscosity.

5.5.4 Comparison between the optimum VES and Wintershall's proprietary VES

Winter shall, the German E& P Company that has been declared as the 2013 winner for the EOR projects have been implementing steam flooding at Emlichheimin oil field since 1981. In addition, they worked extensively with BASF, the reputed chemical company for developing advanced chemical EOR fluids in more challenging conditions. One such advancement is the VES flooding using proprietary Triphenoxy methanes (TPM). TPM are the special and unique classes of surfactant possessing compact hydrophobic head and three flexible hydrophilic tails. Commercial viscoelastic surfactants have short hydrophilic head and long hydrophobic tail. We are comparing the performance of their proprietary TPM and our VES-OPT based on the recovery potential and operating conditions in the **Table 16**

Table 16: Comparison between Triphenoxymethanes and VES OPT

System	VES	VES (Our Work)
Surfactant	Triphenoxymethanes	(Armovis)
Temperature,℃	55	80
Salinity, mg/L (ppm)	186000	57000 S.W and 213,756 F.W
Injection rate ml/h	9	24
Rock type	Sandstone	Carbonate
Permeability (milli Darcy)	2000	110
Oil type	Bockstedt oil	Crude oil with 12 cP
Recovery	Brine flooding gives S_{or} to 0.416 VES flooding reduces S_{or} from 0.416 to 0.35	Brine flooding gives S_{or} of 0.647 VES flooding reduces S_{orr} from 0.421 to 0.23.
Reference	(Brand, Hansch et al. 2014) SPE 169689,	This work, 2014

The **Table 16** compares the performance of core flooding using the optimum VES in this research with the proprietary viscoelastic surfactant from Wintershall. Though the consumption of Armovis used in this research is higher with 1.5 PV of 0.5%, the conditions used in this research is harsher than the one used with 1 PV of 0.23% of TPM. 113 milli Darcy carbonate formation is easily the tougher candidate for chemical EOR method than 2 Darcy sandstone reservoirs. Temperature of 80℃ is far higher than 55℃. TPM is the proprietary based surfactant exclusively developed for EOR by Wintershall in conjunction with BASF. Armovis (VES-OPT) is an advanced well stimulation fluid developed by Akzonobel. Still VES-OPT used in the research competed with the TPM in

terms of EOR applicability. The major difference between well stimulation fluid and EOR fluid is the ability of the EOR fluid to sustain the hostile reservoir conditions for a longer period of time and has been reported in the previous section 5.4.3 titled optimization of thermal stability.

5.5.5 Comparison between various EOR methods

The applicability of chemical EOR methods in carbonate reservoir is comparatively lesser than in sandstone reservoirs (Manrique, Thomas et al. 2010) . The challenges precluding the applicability of chemical EOR methods in carbonate reservoirs are the harsh conditions such as high salinity, high divalency, high temperature and heterogeneity in the form fractures, low permeability, strong capillarity etc. Recently several EOR methods were tested on the lab scale. It includes VES flooding in this thesis. It also include surfactant polymer flooding (Yousef, Al-Salehsalah et al. 2011; Han, AlSofi et al. 2013) , smart water flooding (Yousef, Al-Salehsalah et al. 2011), chelating agent EOR (Abdelgawad, Mahmud 2014). These EOR methods are designed to combat issues with the harsh conditions. However heterogeneity problems were not explored in the lab scale studies. In this section, the comparison is made VES and other EOR methods based on the incremental recovery, conditions on the lab scale. Most importantly, certain problems associated with these EOR methods due to heterogeneity that were often overlooked in lab-scale studies is elaborated in this section along with the solution that VES could provide. To advocate the potential of VES to combat those problems, the recommendations were made for future studies in section 7.2.

5.5.5.1 VES vs Surfactant-Polymer system

VES flooding with 1.5 PV gives the incremental recovery of 29.35% after water flooding at the temperature of 80℃ and the salinity of 57000 ppm. Surfactant polymer flooding gives the additional recovery of 18% at 95℃ and 57000 ppm (Han 2013). VES flooding gives higher incremental recovery than SP flooding. But the operating condition of SP flooding is slightly harsher than VES flooding. Also the consumption of SP slugs is lower than VES. However, SP flooding employing two different chemicals is susceptible in terms of compatibility. Incompatibility between them may affect its interfacial and mobility control property. Ultimately it may lead to the lower recovery that could not be captured in short-scale and short term core flooding.

Overlooked problems in SP flooding

Carbonate reservoirs being characterized by heterogeneity and capillarity need both mobility control and mobilization from the EOR slug. Surfactant flooding alone would not be effective in heterogeneous carbonate reservoirs. It is due to the low viscosity of surfactant that could lead to channeling, adverse mobility ratio and poor low sweep efficiency. Polymer flooding alone leads to lower displacement efficiency due to the inability of polymer to reduce the IFT or capillary force. Surfactant cannot generate viscosity and polymer cannot provide IFT reduction. Multiple slugs including surfactant and polymer together are capable of providing both microscopic mobilization and macroscopic sweep. But there exists the problem of separation with the injection of multiple slugs (Li, Shi et al. 2009) that is often overlooked in lab-scale studies. These problems may not be traceable with short scale core flood. The recovery factor estimated

with the short term core scale flood may be often overestimated. In surfactant-polymer flooding, surfactant and polymer are prone to separation (Shah 1977), (Sheng 2010), (Lyons and Plisga 2011). The efficiency of surfactant polymer system in recovering the residual oil with 30cm core is less than with 90cm core (Hesselink and Faber 1981). In surfactant-polymer flooding, favorable mobility ratio has to be maintained between the oil bank and chemical slug. Controlled mobility ratio should also be maintained between the chemical slug and mobility buffer (Green and Willhite 1998). Polymer can be injected as the pre slug to surfactant or along with surfactant as the single slug or can be injected as the follow-up buffer slug to surfactant. In each case, stability between the surface active surfactant and polymeric materials is important. But it is not guaranteed that the slugs will remain intact throughout the flooding.

Surfactant polymer interaction (SPI) is the unwanted interaction between surfactant and polymer (Shah 1977). Polymers are prone to Inaccessible pore volume (IPV) problems because of its high hydrodynamic radius (Sheng 2010). Because of IPV, polymer slug will not get trapped and will move slowly and steadily and may invade the surfactant slug to reach the oil bank. Also because of IPV of polymer, surfactant tend to get trapped more and would result in higher loss than estimated by static adsorption (Shah 1977). If polymer sweeps the oil zone without having enough surfactant, swept oil cannot be mobilized. The diminished surfactant concentration might cause the surfactant to channel thus causing the poor sweep as well. Thus both microscopic displacement and macroscopic sweep efficiency would be affected even with the injection of multiple slugs that are prone to separation. Carbonate reservoirs in particular need both sweep and displacement from the injection slugs on a long term. The recovery factor estimated with

the short term core scale flood may be often overestimated because of the inability of the short scale core studies to capture the problems associated with multiple slug injection.

How VES could help?

Separation between the slugs designed for mobility control and mobilization is deemed to the problem. Injecting surfactant alone or polymer alone cannot give higher recovery particularly in carbonate reservoirs where the need for mobility due to heterogeneity and mobilization due to capillarity is mandatory. VES capable of providing dual function of IFT reduction and viscosity (section 5.3.5) could be a potential option. VES being a single slug doesn't carry the risk of separation associated with the injection of multiple slugs. It is recommended for future studies in section 7.2 to carry out the series of core flooding with the SP system by varying the core length to capture the SPI problems with SP systems. A comparative core flooding studies should be carried out with VES systems at the same conditions with those cores. It is expected that recovery factor with VES flooding would remain the same irrespective of the core length and recovery factor with SP system might go down with the increasing core length. That would clearly give the overestimation of the recovery with SP flooding and potential of VES to combat it.

5.5.5.2 VES flooding vs chelating agents

VES flooding with 1.5 PV of 0.5% of VES gives the incremental recovery of 29.35% after water flooding at the temperature of 80℃ and the salinity of 57000 ppm. Chelating agent flooding with 6 PV of 5 wt. % chelating agent gives the additional recovery of 20.16% at 100℃ and 57000 ppm (Abdelgawad 2014). Incremental recovery with lesser consumption favors VES applications. However, the chelating agents are cheaper than

VES. But Chelating agents flooding are susceptible to certain problems that are over looked in short term core scale flooding.

Overlooked problems with chelating agents

Carbonate reservoirs are heterogeneous (Ehrenberg and Nadeau 2005) characterized by irregular distribution of high permeable zones such as fractures, vugs, thief zones and low permeable regions such as matrix, tight zones in pore throat etc. An injected EOR slug unless viscous would always tend to move through the least resistive, high permeable zone. Usually low permeable regions are highly porous and saturated with oil that would not be swept by the preferential channeling. Chelating agents are not the viscous substance. It could generate viscosity to a minute extent only in the presence of cations and at very high concentration. Chelating agents are prone to channeling through the fractures of carbonate reservoirs and would result in drastic reduction of sweep efficiency and hence the displacement efficiency. The recovery factor attained with short term, core scale studies are overestimated as the heterogeneity level in the core scale is much smaller than the heterogeneity in field scale carbonate reservoir. Overestimation of the recovery factor in core scale studies is due to the fact that sweep efficiency would be almost 100% with the 12 inch core. Heterogeneity affects the sweep efficiency. It is the sweep efficiency which is more important at-least initially than displacement efficiency.

How VES could help?

VES is living polymer which can work in accordance to the existing situation. It can expand in stress-free high permeable zones and it can constrict in stress low permeable

zone. VES is held by weak intermolecular force that leads to reversible shear thinning as discussed in section 5.1.2.2 facilitates could facilitate this. VES can block the fracture and divert the approaching fluid to low permeable zone. This has been reported using micromodel studies (Chabert and Morvan 2010). Micromodel with dual porous system was used by the authors. Matrix has the permeability of 4 Darcy and 80% porosity and fractures have the permeability of 100 Darcy and 20% porosity. Initially, conventional surfactant (Dodecyl benzene sulfonate) was injected as the initial slug and it recovers the 20% oil in the fracture. It has to be noted that fracture is highly permeable and doesn't contain any capillarity and hence displacement efficiency is 100% and it recovery all the oil in fractures. However, the oil in the matrix remains unswept and immobilized. Secondly, VES (Erucyl amido propyl betaine) was injected and only the fractures were swept by he injected VES. It is due to preferential movement of VES towards high permeable region. No additional recovery was achieved with the injection of second slug. The injected conventional surfactant couldn't provide resistance to the approaching VES in the fracture. Having injected the VES into the fracture, the third slug is again injected in the form of conventional surfactant. Third slug was diverted into the matrix zone by the VES which has sealed, solidified and blocked the fractures. VES's elasticity is the reason for this diversion phenomenon. VES's elasticity is ascertained rheologically in section 5.1.5.3. Carbonate reservoirs are naturally fractured and it is characterized by dual porosity system. The short scale core level studies could not capture it and the recovery attained with less viscous chelating agents is overestimated. It is recommended to conduct series of core flooding experiments with VES in the fractured cores. The recommendation is made in section 7.2.

5.5.5.3 VES vs Smart water flooding

VES flooding with 1.5 PV of 0.5% of VES gives the incremental recovery of 29.35% after water flooding at the temperature of 80℃ and the salinity of 57000 ppm. Smart water flooding with the step wise decline in salinity gives the additional recovery of 18% with carbonate core. Recovery factor is higher with VES. Both VES flooding and smart water flooding are expensive. Smart water flooding just like chelating agents flooding are prone to problems that is overlooked.

Over looked problems in smart water flooding

Smart water flooding is nothing but the water flooding with the reduced salinity that could favorably change the wettability of the carbonate reservoirs. Smart water flooding would give low viscous force. Viscous force is needed to get higher capillary number. Smart water flooding works only by altering the wettability. This is the rock-fluid interaction that could increase the higher capillary number and hence the displacement efficiency. Fluid-fluid interaction is also crucial to attain higher capillary number and it cannot be expected from smart water flooding. IFT of smart water is almost 400 times higher than VES (Yousef, Al-Salehsalah et al. 2011) , section 5.3.5. These are perceived to be the reasons for the lower recovery factor with smart water flooding than VES flooding. So, the displacement efficiency itself would not be too high. Importantly, water being a less viscous fluid would not provide any mobility control that is needed in heterogeneous carbonate reservoirs. It would result in drastic reduction in sweep efficiency that the lab scale core could not capture.

How VES could help?

VES can reduce IFT, provide viscous force and may change the wettability as well. But the tests need to be conducted on that perspective for which the recommendations are made in section 7.2. So VES may provide better displacement efficiency than smart water through fluid-fluid interaction and fluid-rock interaction. Additionally, VES can provide much higher sweep efficiency than smart water flooding because of WLM. VES can work with fractured carbonate reservoirs due to its excellent properties that have been discussed in the section 5.5.5.2. Dynamic rheological studies were in favor of VES's potential to exploit fractured reservoirs as discussed in section 5.1.5. Recommendations for future studies in this regard are made in section 7.2.

CHAPTER 6

VES for Complex Heavy Oil Reservoir, a Simulation study

This chapter starts with the brief introductory discussion about the dual mobility control concept in section 6.1. Reservoir simulation studies using ECLIPSE had been carried out to investigate the problems involved in the recovery of heavy oil from complex heavy oil reservoirs. The details about the simulation model are described in the methodology section 3.11. Thin viscous heavy oil reservoirs constitute the complex heavy oil reservoirs which preclude the conventional heavy oil recovery technique's applicability. The efficiency of steam flooding and polymer flooding, the major thermal and non-thermal method is investigated in sections 6.2 and 6.3. The reasons for poor performance of steam flooding and polymer flooding in complex reservoirs are elaborated in sections 6.2 and 6.3. Thickness and the oil viscosity are the factors limiting their applicability. The potential of hybrid method employing VES/Hot water to recover heavy oil through dual mobility control concept is ascertained. VES considered for this hybrid techniques should be thermally stable and should not lose its viscosity drastically upon contacting heavy oil. The principle of hybrid method is that added hot water reduces the heavy oil viscosity, while the thermally stable VES sweeps, drags and displaces the heated less viscous oil due to its viscosity , elasticity and IFT reduction capability. However, the extent to which heavy oil thins because of hot water heating is a complex phenomenon and a sensitivity study has been carried out to study the different cases of viscosity reduction in section 6.4.1. Finally, considering the worst case with higher oil viscosity and lower reservoir

thickness, the comparative studies were made between steam flooding, polymer flooding, hot water flooding and two scenarios of VES/hot water flooding in section 6.4.2.

6.1 Dual Mobility Control, a Novel Concept

Most of the experimental studies were done based on the sort of capillary number as described in section 5.3. However mobility ratio concept discussed in section 1.5 is another important EOR concept which is more of concern in heavy oil recovery. In heavy oil recovery, the viscosities of both the displacing and displaced fluids are very crucial unlike in conventional oil recovery where the viscosity of injection fluid alone is crucially essential for providing the higher viscous force that could increase the capillary number as stated in section 1.5 to increase the recovery factor.

Mobility ratio should be less than 1 for favorable recovery and it could be achieved in heavy oil reservoirs by employing steam flooding to reduce the oil viscosity and by employing polymer flooding to increase the injection slug viscosity. We are proposing the novel concept by which both the reduction of oil viscosity and increment of injectant viscosity are achievable simultaneously. This is called dual mobility control concept which could mitigate the problems associated with the steam flooding and polymer flooding in thin, viscous heavy oil reservoirs.

6.2 Effect of Thickness on Steam flooding

The reservoir and fluid properties used in the construction of steam flooding model is described under the methodology section 3.11 in **Table 5.** The operational parameters are described under the same section are in **Table 6.** The thickness of the reservoir is the only

parameter that was varied from 20ft to 200ft in this study. Oil viscosity was set at 3000 cP. The **Figure 68** depicts the effect of thickness on the total recovery of steam flooding. Steam flooding is the thermal EOR process that uses the heat in the form of steam to reduce the viscosity of viscous heavy oil to enable its mobility. In other words, it keeps the mobility ratio intact by lowering the denominator term in Equation 2, the oil viscosity. However, certain parameters affect the performance of steam flooding and thickness is one such parameter which was investigated. More than 80% of western Canadian heavy oil reservoirs accounting for 1.3 trillion barrels have thickness of less than 16 ft. As it seen, the efficiency of steam flooding drops drastically if the reservoir possesses low thickness. The recovery attained with the reservoir thickness of 200 ft is almost 10 times higher than the one attained with 20ft reservoirs.

Why there are under burden and over burden heat losses and how it affects the performance of steam flooding?

The failure of steam flooding in thin heavy oil reservoirs could be attributed to under burden and over burden heat losses which were documented in literatures (Dyer, Huang et al. 1992). The thin reservoirs possess high surface area when compared with consolidated thick reservoirs. The injected steam tends to heat the thick reservoir by conduction throughout. However as the surface area is higher for thin reservoirs, they are prone to heat losses vertically. Steam being lesser dense tends to overrun towards the over burden rocks and could lose its heat energy in the form of convection to its upper environment, leaving only a portion of heat available for heating the reservoirs horizontally through conduction. Thus injected steam losses the heat to under burden and over burden non-reservoir rock thereby heating the reservoir and its residential heavy oil

inefficiently with diminished steam quality. The inefficient heating leaves the heavy oil still immobile and should have resulted in unfavorable mobility ratio. Unfavorable mobility ratio in turn results in poorer sweep efficiency and hence the recovery efficiency which is the product of sweep and displacement efficiency is on the much lower side for thin reservoirs.

What if the permeability is high in thin heavy oil reservoirs?

Higher permeability is always a desired parameter for any EOR process. As low thickness of the reservoirs hampers the performance of steam flooding, would the increasing the permeability by some means could combat it? To ascertain it, another case was run with the same reservoir and operational as mentioned in previous case except by increasing the permeability of the reservoir rock from 1500 mD to 3000 mD. **Figure 69** compares the performance of steam flooding in heavy oil reservoirs with two different permeability ranges of 1500 mD and 3000 mD. The thickness of the reservoir is varied from the 20ft to 200 ft. As it seen from the **Figure 69**, at higher thickness of 200 ft, increasing permeability to 3000 mD gives the drastic improvement in recovery than at 1500 mD. However, at lower thickness of 20ft, there is a slight improvement recovery while increasing the permeability. This implies that higher permeability will help the steam flooding in heavy oil recovery as long the thickness is high. For thin heavy oil reservoirs, increased permeability doesn't help and hence it is not recommended to consider any fracturing operations for such reservoir whose concern is the heat losses. Hence the low thickness and the subsequent heat losses are the critical parameter and issues associated with the development of thin heavy oil reservoirs.

6.3 Effect of Oil Viscosity on Polymer flooding

The **Figure 70** depicts the effects of oil viscosity on polymer flooding. Polymer flooding belonging to chemical EOR method is major non-thermal method for developing heavy oil reserves. Polymer flooding provides effective mobility control by increasing the viscosity of the injectant fluid thereby injected front moves slower than the displacing front. In other words, it keeps the mobility ratio intact by increasing the numerator term in Equation 2, the injected water viscosity. As seen from the **Figure 70,** the polymer flooding performs better while sweeping the low to moderate viscous oil. Its ability to push the high viscous oil becomes poor. It is clearly evident, that as the oil viscosity increases above 1000 cP, the recovery becomes lower. Total oil recovery corresponding to the oil viscosity of 3000 cP and 6000 cP is almost 13 times and 24 times lower than the recovery 150 cP oil. The attributed reason is viscous fingering of the injected slug. Due to drastic difference in viscosity between the displacing polymer and displaceable viscous heavy oil, the instability evolves at the displacement front in the form of penetrating fingers that could lead to early breakthrough (Homsy 1987),(Sajjadi and Azaiez 2012). The reservoir and fluid properties used in the construction of polymer flooding model is described under the methodology section 3.11 in **Table 5.** The operational parameters are described under the same section in **Table 6.** The oil viscosity of the reservoir is the only parameter that is varied from 100 cP to 6000 cP in this study. The thickness of the reservoir is 200 ft.

Why there is viscous fingering and how it affects the performance of polymer flooding?

Whenever the less viscous fluid displaces the more viscous one, the interface between the less and more viscous fluid doesn't remain flat and hence the piston like displacement contributing to higher sweep efficiency cannot be expected. Instead, for the available pressure difference, the tendency of less viscous, polymer slug to move is more pronounced than the oil, thus resulting in the deformation of interface into fingers that creates its own path towards the production well through the viscous oil without contacting the most of the oil bearing reservoir portion. The schematic of viscous fingering (Jha, Cueto-Felgueroso et al. 2011) is shown in the **Figure 71**.

Because of the intrusion of polymer (yellow portion) into the high viscous crude (Black portion), adverse mobility ratio would be created and could result in the poor sweep efficiency. Thus the overall recovery is low for high viscous oil with polymer flooding. One way to combat is to increase the viscosity of injected polymer higher than that of crude oil which is highly impossible if the crude viscosity is in higher range of 2000 cP or more. The best solution is to reduce the oil viscosity without compromising the heat losses problems associated with thermal methods and hence the formulation of VES/hot water is proposed which is discussed in detail in the section 6.4.

What if the permeability is high?

Higher permeability is always a desired parameter for any EOR process. As higher oil viscosity of the oil hampers the performance of polymer flooding, would the higher permeability combat it? To ascertain it, another case is run with the same reservoir and

operational parameters as mentioned in previous case except by increasing the permeability of the reservoir rock from 1500 mD to 3000 mD.

The **Figure 72** compares the performance of polymer flooding in heavy oil reservoirs with two different permeability ranges of 1500 mD and 3000 mD. The viscosity of the oil is varied from the 150 cP to 6000 cP. As it seen from the **Figure 72,** the recovery is slightly higher for higher permeability. This could be due to the fact; higher permeability might have increased the injectivity thereby the facilitating the reservoir to intake more volume of polymer that could provide additional viscosity to the displacing slug to combat viscous fingering to little extent. However that little extent is not at all sufficient as the viscous fingering becomes dominant with time and affecting the recovery drastically at higher oil viscosity.

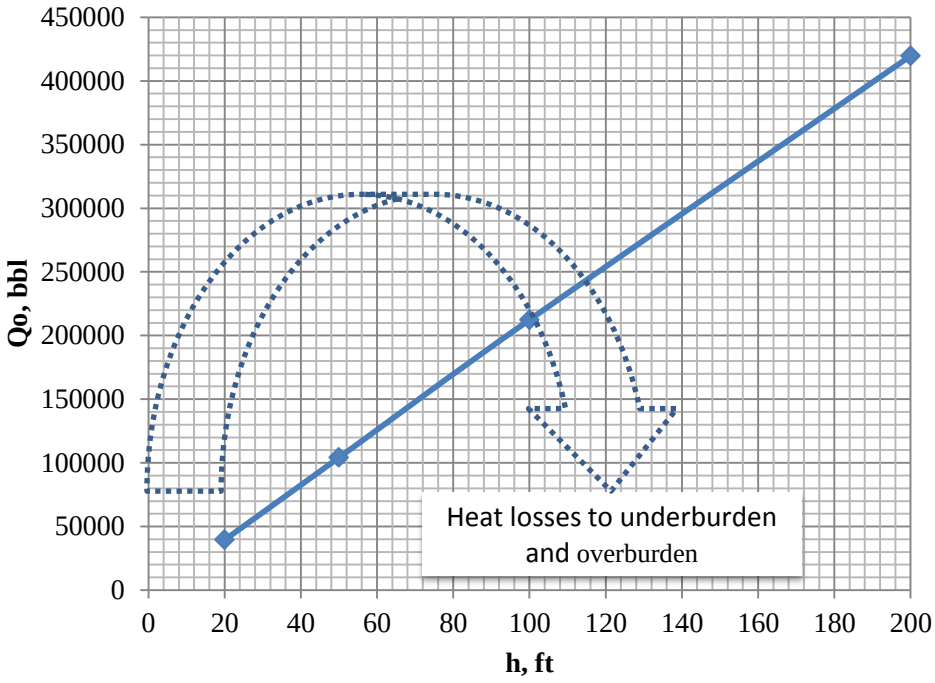


Figure 68: Effect of thickness on steam flooding

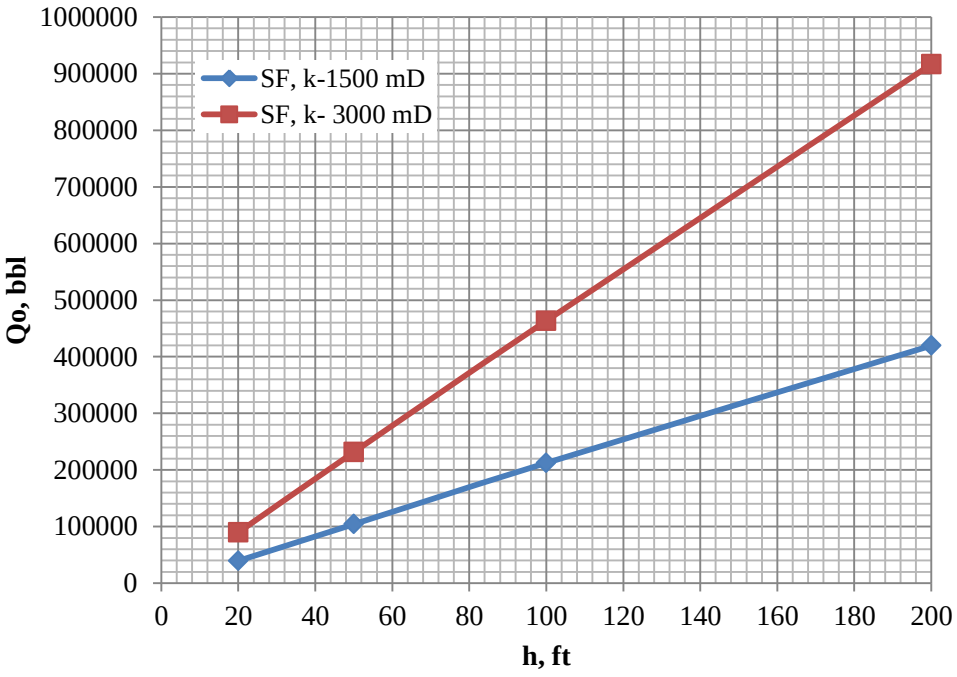


Figure 69: Effect of increasing permeability on steam flooding in heavy oil reservoirs

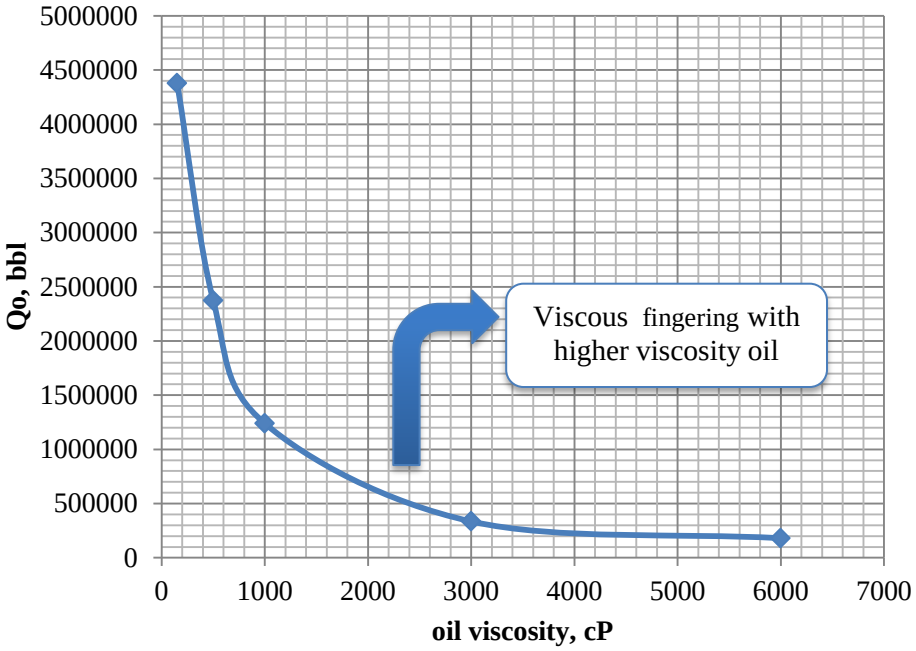
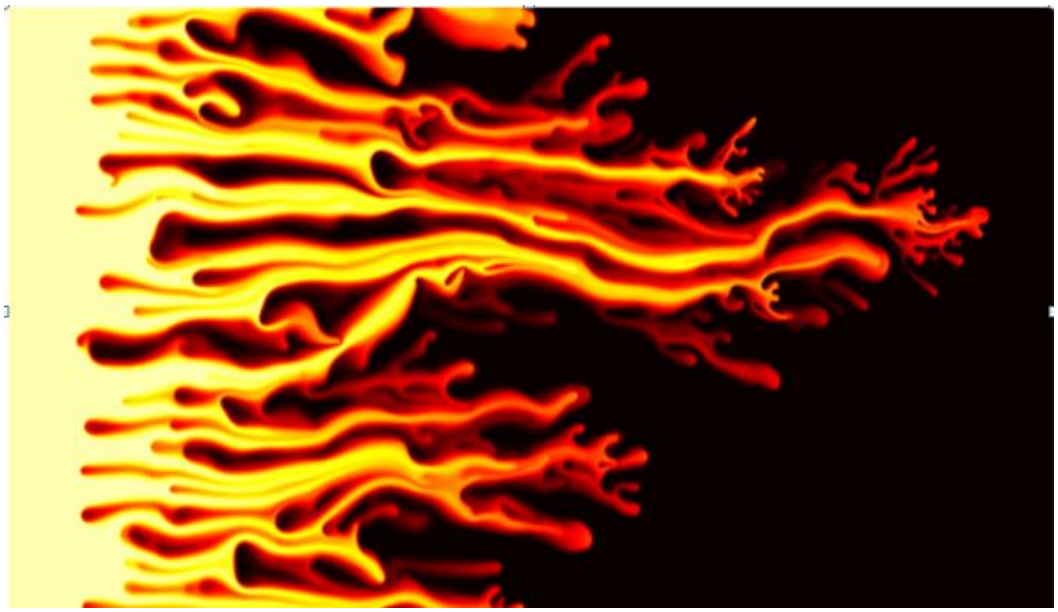


Figure 70: Effect of oil viscosity on polymer flooding



Jha, 2011

Figure 71: Viscous fingering of less viscous fluid into the more viscous fluid

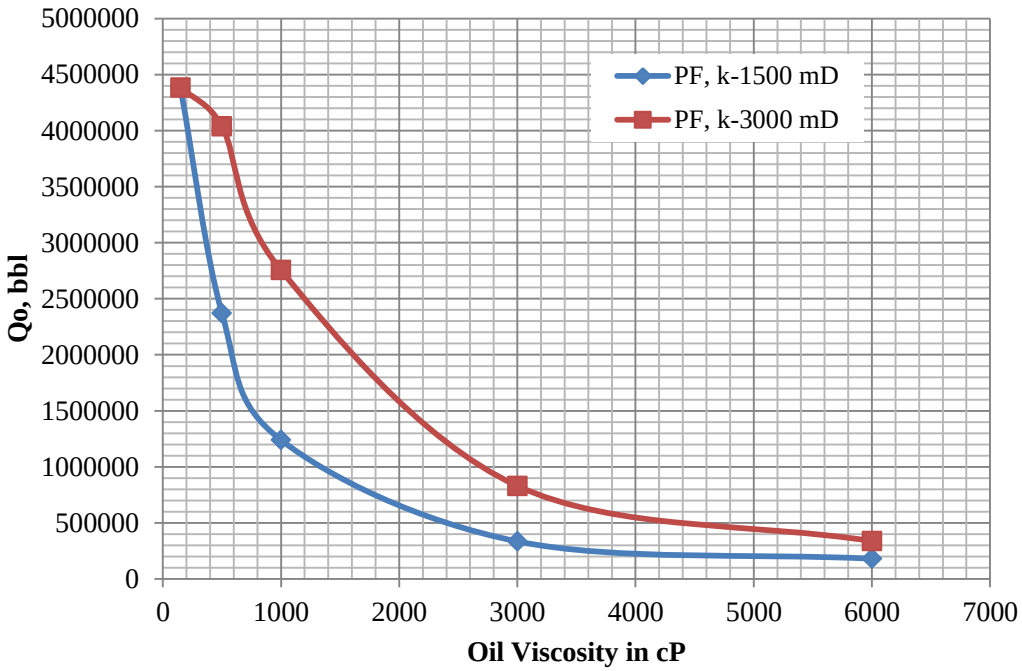


Figure 72: Effect of increasing permeability on polymer flooding in heavy oil reservoirs

6.4VES/Hot water flooding to combat issues associated with Steam flooding and Polymer flooding

It has been discussed that the steam flooding becomes ineffective in thin heavy oil reservoirs and polymer flooding becomes inefficient in viscous heavy oil reservoirs. The reasons are discussed. More than 80% of western Canadian heavy oil reservoirs accounting for 1.3 trillion barrels have thickness of less than 16 ft and oil viscosity ranging from 600 cP to 40000 cP (Adams 1982), (Delamaide, Zaitoun et al. 2014). The applicability of steam flooding is limited to reservoir with thickness above 20 ft (Taber, Martin et al. 1997) and the applicability of polymer flooding is limited to reservoir containing oil whose viscosity is not above 150 cP. In this section, we are trying to combat the issue of heat losses and viscous fingering associated with both the EOR methods by considering the worst scenario with low thickness of 20 ft and higher oil viscosity of 3000 cP.

We are proposing the novel hybrid technique employing hot water / VES that could potentially decrease the oil viscosity to an extent that could be swept and displaced by the VES easily. It is based on dual mobility control concept (Azad, Sultan et al. 2014). The injected hot water reduces the oil viscosity and reduction in oil viscosity is an implicit function dependent on several parameters. Two cases have been considered in this section.

6.4.1 Effect of Viscosity Reduction on Oil Recovery during VES/hot water flooding

A series of viscosity reduction of heavy oil has been considered ranging from 1500 cP to 50 cP to see the effect on corresponding recovery. As mentioned in the methodology section 3.11, VES/hot water flooding is simulated from polymer flooding by incorporating surfactants effects into it and assuming that all the properties are thermally stable in the presence of hot water. Steam flooding mode was activated for 2 years to reduce the oil viscosity and then followed by VES/hot water for 18 years. In the course of 18 years flooding, VES/hot water is injected for 6 months followed by hot water alone for 6 months.

The **Figure 73** depicts the different level of oil recovery attained VES/hot water flooding corresponding to the viscosity reduction of the heavy crude oil. As it is seen from the **Figure 73,** higher the viscosity reduction, higher the recovery. As oil becomes less viscous, VES can contribute to recovery through IFT reduction, shear thinning, viscoelasticity, mobility control etc. But the extent to which the hot water can reduce the crude oil viscosity is unknown; so, two cases from this study were considered for the next discussion along with full scale steam flooding, polymer flooding, and hot water flooding.

6.4.2 Comparison between Steam flooding, Polymer flooding, hot water flooding and VES/HOT water hybrid EOR

The reservoir and operational parameters used in simulating the steam flooding, polymer flooding, hot water flooding are mentioned in **TABLE 5, 6**. As discussed in section 6.4.1,

VES/hot water flooding is simulated from polymer flooding model by incorporating surfactants effects into it and assuming that all the properties are thermally stable in the presence of hot water. Steam flooding mode was activated for 2 years to reduce the oil viscosity and then followed by VES/hot water for 18 years. However, two cases of oil viscosity reduction from **Figure 73** are considered. In one case, the viscosity of oil is assumed to be dropped from 3000 cP to 200 cP and in another case, viscosity of the oil is assumed to be dropped from 3000 cP to 1500 cP.

The **Figure 74** compares the performance of steam flooding, polymer flooding, and hot water flooding along with 2 cases of VES/hot water flooding (with 200 cP oil and 1500 cP oil). As it seen from the **Figure 74,** VES/hot water flooding outperforms steam flooding, polymer flooding and hot water flooding respectively. Steam flooding should have undergone severe heat losses in 20ft reservoirs. Polymer flooding should have undergone viscous fingering with 3000 cP oil. Hot water flooding performs slightly better than steam flooding. It is due to the higher viscosity of hot water than steam thus providing larger displacement drive (Diaz-Munoz and Ali 1975). Secondly hot water permit the use of higher injection pressure than steam flooding at the given temperature might give better sweep efficiency. Hot water flooding is the least expensive thermal EOR method (Ali 1974). However, the hot water doesn't heat the reservoir and its oil much; hence one cannot expect the higher recovery associated with it especially for viscous heavy oil reservoirs as seen from **Figure 74**. Still attaining the favorable mobility ratio of less than 1 is a challenge with hot water. So a mobility control agent incorporated along with hot water slugs might help. Hot water – surfactant EOR process was patented (Dilgren and Owens 1979). Surfactant generates foam which increases sweep efficiency.

However, foam collapse in accordance to the heat loss rate. Heat loss rate in thin heavy oil reservoirs with high surface area is high making foam an ineffective mobility control agent for thin viscous heavy oil reservoirs.

The undisputed superior performance of the proposed hybrid EOR techniques employing VES/hot water flooding based on dual mobility control is clearly evident from the **Figure 74.** This synergism is possible only with thermally stable VES that could sustain the harsh conditions while injected in tandem with hot water. Unlike the conventional surfactant that generates susceptible foam, VES generates WLM in hot water and could viscosify it. Thus it is the viscous hot water flooding combining the advantage of viscosity for sweep and heat for viscosity reduction. Further, VES reduces the IFT of heated less viscous oil providing an additional contribution to displacement efficiency. VES also pulls the heavy oil by its dragging mechanism due to viscoelasticity (Morvan, Degre et al. 2012). Displacement mechanisms due to viscoelasticity are more decisive than ultra-low IFT reduction in ASP flooding (Hou, Liu et al. 2001). VES are known for thermal stability (Berger and Berger 2008), (Brand, Hansch et al. 2014), (Degré, Morvan et al. 2011). It could be remain viscous for 6 months at 150℃ for 6 months(Watkins 2009). It is to be noted that even while considering the worst case of VES/Hot water flooding with the drop in viscosity of oil from the initial value of 3000 cP to 1500 cP is just 50%, yet the recovery is way higher when compared with the case involved the polymer flooding or steam flooding of 3000 cP oil. Hence this strongly advocates that viscous fingering associated with polymer flooding can be mitigated by this synergistic hot water / VES flooding. The hot water in interface between injected viscous hot water and heavy oil heats the oil, reduces the oil viscosity and avoid or reduce the fingering

associated with the viscosity contrast between the injected slug and heavy oil. Simultaneously the injected hot water doesn't raise the reservoir temperature by much (Zhao and Gates 2013) and hence resulting in the lower heat losses than steam flooding and therefore combating the heat losses associated with steam flooding in thin heavy oil reservoirs.

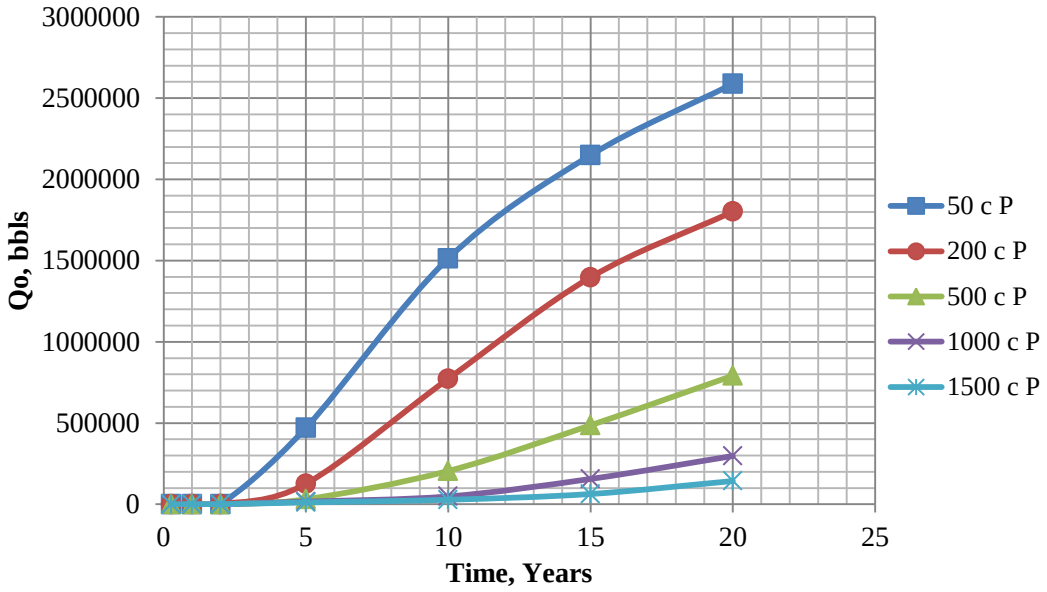


Figure 73: Effect of viscosity reduction due to hot water / VES flooding on oil recovery

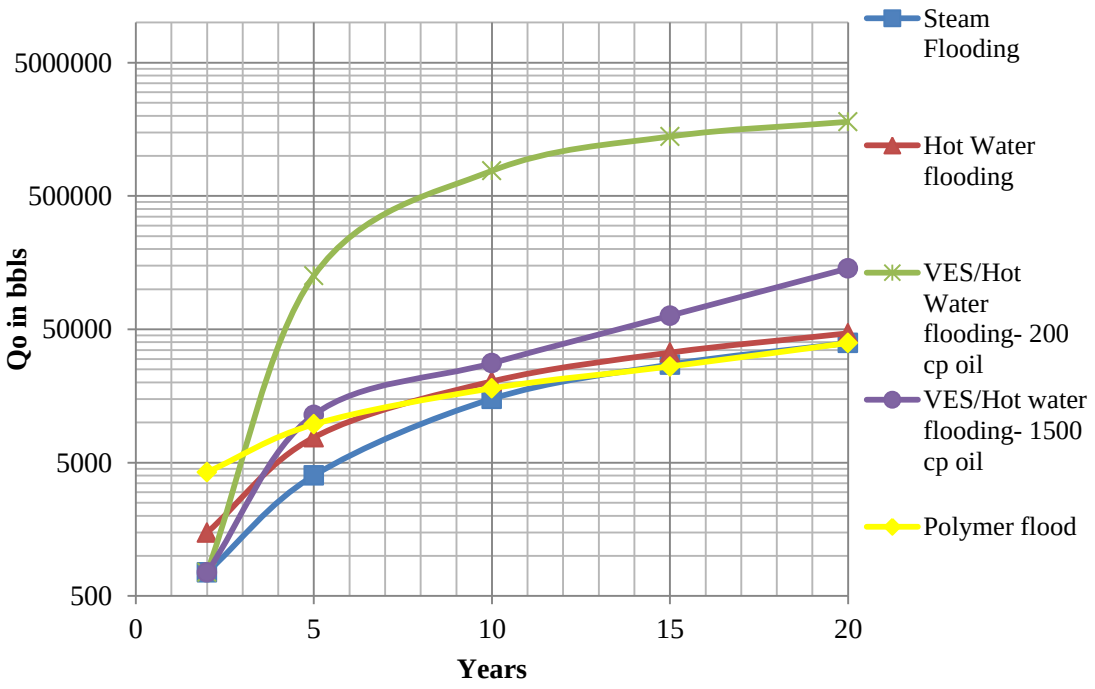


Figure 74: Comparison between SF, PF, and Hot water flooding, VES/hot water flooding

CHAPTER 7

Conclusions and Recommendations

7.1 Conclusions

Following conclusions were made upon evaluating the potential of studied systems for chemical EOR applications in carbonate reservoirs.

1. Among the three surfactants screened initially for its viscoelasticity, Armovis performs better as an EOR fluid at 57000 ppm salinity by providing both viscosity and IFT reduction.
2. Rheological studies conducted on the optimum VES indicate that Wormlike micelles formed by self-assembly of VES is very sensitive to concentration, temperature, flow rate and salinity. The reasons are ascertained.
3. A comparative study between polymer and VES revealed the potential advantage VES possess over polymer due to its flexibility. Certain tight portion of reservoirs can really be explored by VES due to its better shear thinning ability to relieve stress temporarily unlike rigid polymers. Thus VES can be a better mobility control agent sweeping every nook and corner of the reservoir upon complete characterization and optimal development.
4. Further the dynamic studies coupled with shear studies conducted sequentially revealed the possibility of enhancing chemical EOR applicability in fractured

reservoirs. Viscoelasticity of VES is high that it could drag the residual oil thereby could contribute to additional recovery mechanism apart from macroscopic sweep and microscopic displacement.

5. The ability of VES to retain its function even upon contacting connate formation water is also noticed visually. The rheological studies also confirm that VES can retain WLM even upon contacting formation water.
6. The effect of parameters on IFT reduction of VES is also studied and it revealed that VES could be an effective displacement agent in harsh conditions.
7. VES, S/VES and VES/P systems studied for its recovery potential to provide dual function of increasing macroscopic driving force and decreasing microscopic resistive force revealed that VES as a single system outperform the other two systems.
8. S/VES is the complete failure irrespective of class of surfactants added to it. It severely interfered with WLM formation and hampers the performance of VES. VES being a parental surfactant doesn't accept any more surface active agents that affect its packing parameter.
9. VES/P performs better than S/VES and it can be a potential system if the components of oil affect the VES's WLM and if the oil viscosity is high. However, the applicability of VES/P system has to be the expense of diminished IFT reduction of VES. Long term thermal stability should also favor VES/P formulation by not letting the phase separation between the components. However VES/P systems studied in this research got separated and hence not recommended.

10. Thermal stability tests conducted on long scale revealed the inability of VES to sustain its WLM and its associated unique properties at harsh conditions. However, the positive point that can be taken from the poor thermal stability of VES in terms of EOR perspective is that hostile aging could act as an internal breaker for VES that could be used for plugging the high permeable streaks and diverting the slugs towards low permeable region. An astutely formulated VES/R system combat the issues associated with poor thermal stability of VES while aging at high temperature. VES/R system exhibit excellent thermal stability at 65℃ and good thermal stability at 95℃.
11. Core flooding studies conducted on a 113 milli Darcy core reveal the excellent recovery potential of VES. VES provide the incremental recovery of 29.35%. VES as single fluid possess several beneficial properties that could increase the recovery factor in multiple ways. It include
    a. IFT reduction for mobilization
    b. shear viscosity for mobility control
    c. shear thinning for penetrating and mobilizing the oil in low permeable regions
    d. Viscoelasticity for oil dragging recovery mechanism in low permeable region
    e. Preferential movement towards oil.
12. High salinity, low permeability, fractures, high temperature and strong capillarity are complicating factors limiting the applicability of chemical EOR in carbonate reservoirs. VES forming WLM possess the following properties that could

address these challenges and enhance chemical EOR applicability in carbonate reservoirs.

a. Positive influence towards salts combats high salinity problems. VES need salts to screen the repulsion between the head groups to enable the entanglement and carbonate reservoir provide salts. There exists the mutuality between carbonate reservoirs and VES.
b. Shear thinning facilitates easy entry the of fluid into the tight region due to the reptation through Brownian motion and of course reversible due to weak intermolecular force to provide conformance control whenever needed
c. Elasticity for blocking the fractures and diverting the slugs from entering or traversing through fractures. Diverted slugs are forced to go through the low permeable region thereby enhancing sweep efficiency and displacement efficiency
d. Synergism with reducing agent to sustain WLM at high temperature by preserving the highly active, unsaturated, carbon-carbon double bond from Oxidation enables chemical EOR for high temperature applications.
e. Strong capillarity and heterogeneity in the carbonate reservoirs necessitate the need for both mobilization and mobility control and VES as a single system form WLM that provide the dual function of IFT reduction and viscosity. Hence, this obviates the need for multiple slugs that are prone to separation.

13. Reservoir simulation studies conducted give the glimpse of enhancing the recovery of huge heavy oil reserves from complex reservoirs. Thermally stable VES synergizing with hot water provide an opportunity for recovering heavy oil from thin viscous heavy oil reservoirs where conventional steam floods and polymer flooding fails due to heat losses and fingering

7.2 Recommendations

1. The viscosity drop of VES with various type of crude oil should be studied to formulate the optimal VES/P systems. Understanding the molecular interaction between polymer and VES is crucial to get the dual benefits. Certain class of polymer may negatively hamper VES's performance by converting the WLM of VES to spherical micelles as discussed in section 5.1.3. A series of VES/P system with different classes of polymer can be studied to find the optimal one that doesn't affect the IFT of VES as well. Also long term aging has to provide positive results to advocate VES/P systems for EOR.
2. Adsorption could be a problem with VES. Adsorption could be due to the positive influence of VES towards salts. Chelating agents could be an option to mitigate adsorption by deactivating the calcium ions. However, if the chelating agents consume the ions that are needed for WLM, then it is not applicable readily. The best possible solution is to use the sacrificial agents to block the adsorption sites. Since VES is a sensitive fluid, care has to be taken again to ensure the sacrificial agent doesn't affect WLM growth. Sacrificial agent should be cheaper as well. Certain polymer can also act as a sacrificial agent due to it the

competitive adsorption. Hence VES/P system has this advantage too. However, screening the optimal system should be based on IFT reduction, viscosity, adsorption, thermal stability etc.

3. If chelating agent (C) is consuming the ions needed for WLM, then an optimization in terms of slug design should help. C/VES system can be formulated to deactivate the calcium ions by injecting chelating agent as the initial slug followed by VES in calcium-less carbonate formation. Test also has to be conducted to ascertain the optimal mode of preparation. Whether the WLM formed with sea water would be affected if chelating agent is added to it. If it provides the positive result, then C/VES can be injected as the single slug, if not then it has to be separated by mutual spacer in between.
4. Surfactant polymer systems are prone to SPI problems that may reduce the overall efficiency of the process. SPI problems would affect the displacement efficiency and sweep efficiency and hence the overall recovery factor. This may not be captured in the short scale core as discussed in section 5.5.5.1.Hence the series of core flooding with the cores of increasing length should be done to ascertain these problems.

   To combat, VES capable of providing microscopic mobilization and macroscopic sweep as a single slug without carrying the risk of separation is recommended. The same set of core flooding experiments with the same conditions should be carried out to identify the potential advantage that VES possess over SP system especially in lengthier core. Lengthier cores are mandatory to capture SPI problems associated with surfactant-polymer systems.

5. Lab studies doesn't capture the heterogeneity especially the fractures in the short scale cores as discussed in sections 5.5.5.2 and 5.5.5.3.. Hence the recovery attained with the formulated slugs is overestimated. The presence of fractures leads to the channeling of the injected fluids. It leads to low sweep efficiency in low permeable region. But since the fractures could not be incorporated in the lab studies, only the displacement potential of the formulated slugs is ascertained to an appreciable level. Carbonate reservoirs are characterized by irregular fractures and hence it is imperative to consider the core flooding in the lab by incorporating heterogeneity in the form of fractures.

   VES, the proven diverting agent could block the fracture and could improve the pressure drop and could divert the slugs to low permeable region. Smart water, chelating agents and other less viscous EOR slugs could not block the high permeable region. Hence it is highly recommended to conduct the series of the core flooding with VES, chelating agents, smart water in fractured core to ascertain the following

   a. Whether the chelating agent flooding, smart water flooding and VES flooding that gave good recovery in relatively homogeneous core would be able to give the same level of recovery in fractured cores
   b. If the recovery with less viscous EOR slugs is lower in fractured carbonate core than relatively homogeneous core, then all the lab scale studies should incorporate the heterogeneity in the core before advocating their slug's recovery potential in carbonate reservoirs
   c. By the comparing the recovery factor of VES and other less viscous slugs in

fractured cores, the superior potential of VES can be identified with the core studies. Already the rheological studies did in this thesis advocate the potential of VES as seen from section 5.1.5.

6. VES provides IFT reduction and hence it provides fluid-fluid interaction. Contact angle measurement with VES has to be conducted to find whether it could lead to rock-fluid interaction in a favorable manner.
7. VES synergism with hot water could lead to the Hybrid EOR method. Tests has to be conducted to see ,
    a. How much viscosity reduction can the heat from hot water provide to heavy crude?
    b. Whether VES acts as blockage for heat transfer, if so study the structure and rectify it if possible or recommend it to VES manufacturers.
    c. Whether heated crude oil can be mobilized by VES. Viscosity reduction of VES with heavy oil should not be a problem. If it exists, then formulate VES/P/hot water hybrid, so that three could work in tandem.
    d. VES/R system also is a possibility if VES as a single slug is poorly stable thermally
    e. Steam with VES can be also tried as long the VES is thermally stable at steam temperature.
8. Stronger reducing agents can be combined with VES to enhance the thermal stability further for deep reservoir applications.
9. Carbon dioxide flooding has been deemed to the potential method for carbonate reservoirs. It can provide complete miscibility, theoretically IFT would be zero.

However, fractured carbonate reservoirs with irregular thief zones may result in poorer sweep efficiency. VES can acts as the mobility control agent in Carbon di oxide flooding. Experiments need to be conducted for evaluating the potential of VES/CO2 flooding. Miscibility of C02 with oil in the presence of VES has to be tested. Viscosity of VES in the presence of C02 also needs to be tested.

10. VES's potential to redefine EOR screening criteria should be assessed. Screening criteria states that chemical EOR methods are not preferred for carbonate reservoirs. VES can work with carbonate reservoirs as understood from this thesis. If the experimental works were in favor of VES applications in heavy oil and deeper reservoirs, then it can expand the chemical EOR applicability and could redefine the existing EOR screening criteria.
11. The potential of VES as a mobility control agent can be compared with Foam in wide variety of conditions. Surfactant forms foam while VES forms WLM. Foam and WLM provides viscosity for mobility control. However foam is susceptible to salinity in high saline reservoirs and fingering in low permeable reservoirs due to high mobility gas flow. WLM needs salts for its formation and be a living polymer with weak molecular force, it can act in accordance to the reservoir either by deforming or reforming. Hence this could avoid fingering problems. .
12. VES is a living polymer and it performance is based on its structure and the conditions. A reverse methodology can be adopted for enhancing EOR applicability. First prescribe the reservoirs and fluid properties, and then formulate VES accordingly in the lab. This would be of great assistance to complex reservoirs. It's the packing parameter that determines the WLM

formation; strengthening the double bond determines the long term stability, hydrophobicity strength determines the IFT reduction. Design these parameters accordingly by formulating its structure with the help of chemist.

13. Reservoir simulator incorporating the dual function, viscoelasticity and shear thinning is to be built. It would be great, if the molecular modelling is incorporated into it. A series of experiments is to be conducted using VES to build such simulator. A strong collaboration between academic and industrial EOR researchers is mandatory in this regard.
14. VES is a living polymer which can be exploited to the need that the reservoir entails. The precise characterization is essential for it. The most optimal well placement and optimal operational parameters are needed to get the best out of VES's unique properties. Stochastic optimization tools such as covariance matrix adaptation evolution strategy (CMA-ES), particle swarm optimization (PSO) are recommended to trace the most optimum parameters. However, having the relevant simulator is the prerequisite for this.

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